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Presentations at the Conference on Methyl Chloroform and Other Halocarbon Pollutants (Washington, D.C., February 27-28, 1979) are documented. Included among the authors are research scientists, industry representatives, and regulatory officials. The 16 papers fall into 2 basic groups. The first 10 papers present results of research in atmospheric chemistry as related to the question of stratospheric ozone depletion by halocarbons. Drawing upon atmospheric measurements and model calculations, the authors give estimates of emission levels, current atmospheric burdens, tropospheric lifetimes, the importance of sinks, effects on stratospheric ozone, and related questions. The final 6 papers take the perspective of involvement in, or concern with, regulatory decisionmaking. The authors consider various options, recommendations, and plans for halocarbon control in light of available scientific data. Finally, the Panel Discussion which concluded the Conference is presented in verbatim transcript form. Focusing on the current status of atmospheric measurements, the participants discuss problems in obtaining accurate halocarbon data, and discrepancies between and within the results of individual investigators.

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PREFACE

The Clean Air Act gives the U.S. Environmental Protection Agency (EPA) authority to control volatile organic compounds in order to protect air quality. Included is control of pollutants that are sources of tropospheric ozone (O_3) (e.g., high-reactivity organics that produce photochemical O_3) and pollutants such as halocarbons that can, by low reactivity, be transported into the stratosphere and affect the O_3 layer.

The purpose of the Conference on Methyl Chloroform and Other Halocarbon Pollutants was to establish the distribution and persistence of methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF) and other related halogenated organic compounds. The emphasis was largely on the effects of halocarbons on O_3 depletion. MCF was chosen as the principal compound of interest because its production rate is rapidly increasing and there is some doubt as to its tropospheric lifetime. The uncertainty with regard to the lifetime of MCF is largely a result of uncertainty on the amount of hydroxyl radical (OH) present in the troposphere as well as the ambient concentration of MCF. Of course, these are related, since low levels of MCF necessitate high OH concentrations.

Any model which predicts a change in stratospheric O_3 must depend upon product identification, reaction rates, and a mechanism. Therefore, any findings or predictions reported in the following chapters are based on current knowledge of the reaction scheme. The predictions may change as better data become available. As a reminder, remeasurement of the HO_2-NO reaction now leads us to calculate stratospheric O_3 enhancement (instead of depletion) by supersonic transports. However, to the smog chamber modelers, this reaction now leads to an overprediction of O_3, suggesting that there is still something wrong with the proposed NO_x mechanism for describing photochemical smog.

This document reports the findings of experts from research institutions, manufacturers, and government agencies. Hopefully, EPA can use this information to better direct its research efforts and arrive at a reasonable control strategy for MCF and other halogenated organic compounds.

J. J. Bufalini
Environmental Sciences Research
Laboratory

ABSTRACT

Presentations at the Conference on Methyl Chloroform and Other Halocarbon Pollutants (Washington, D.C., February 27-28, 1979) are documented. Included among the authors are research scientists, industry representatives, and regulatory officials.

The 16 papers fall into 2 basic groups. The first 10 papers present results of research in atmospheric chemistry as related to the question of stratospheric ozone depletion by halocarbons. Drawing upon atmospheric measurements and model calculations, the authors give estimates of emission levels, current atmospheric burdens, tropospheric lifetimes, the importance of sinks, effects on stratospheric ozone, and related questions.

The final 6 papers take the perspective of involvement in, or concern with, regulatory decisionmaking. The authors consider various options, recommendations, and plans for halocarbon control in light of available scientific data.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

CAA — Clean Air Act
CARCE — Committee on Alternatives for the Reduction of Chlorofluoromethanes
CEQ — Council on Environmental Quality
CFC — chlorofluorocarbon
CFM — chlorofluoromethane
CISC — Committee on Impacts of Stratospheric Change
CPSC — Consumer Product Safety Commission
DOC — Department of Commerce
DOE — Department of Energy
DOT — Department of Transportation
DU — Dobson Unit
EPA — Environmental Protection Agency
FAA — Federal Aviation Administration
FC-11 — fluorocarbon-11 (trichlorofluoromethane, CCl_3F)
FC-12 — fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2)
FC-14 — fluorocarbon-14 (carbon tetrafluoride, CF_4)
FC-22 — fluorocarbon-22 (chlorodifluoromethane, $CHClF_2$)
FC-113 — fluorocarbon-113 (CCl_2FCClF_2)
FC-114 — fluorocarbon-114 ($CClF_2CClF_2$)
FC-133 — fluorocarbon-133 (CF_3CH_2Cl)
FC-142A — fluorocarbon-142A (CH_3CClF_2)
FC-152A — fluorocarbon-152A (CH_3CHF_2)
FDA — Food and Drug Administration
FY — Fiscal Year
GC — gas chromatography

ICAS — Interdepartmental Committee on Atmospheric Sciences
ICSOP — Interagency Committee on Stratospheric Ozone Protection
IMOS — Inadvertent Modification of the Stratosphere
IR — infrared
ITCZ — intertropical convergence zone
JPL — Jet Propulsion Laboratory
MCA — Manufacturing Chemists Association
MCF — methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3)
MTD — maximum tolerated dose
NAAQS — National Ambient Air Quality Standards
NAS — National Academy of Sciences
NASA — National Aeronautics and Space Administration
NBS — National Bureau of Standards
NCAR — National Center for Atmospheric Research
NCHS — National Center for Health Statistics
NCI — National Cancer Institute
NH — Northern Hemisphere
NIOSH — National Institute of Occupational Safety and Health
NOAA — National Oceanic and Atmospheric Administration
NSF — National Science Foundation
OAQPS — Office of Air Quality Planning and Standards
OPM — Office of Program Management
ORD — Office of Research and Development
OSHA — Occupational Safety and Health Administration
OTS — Office of Toxic Substances
PCE — perchloroethylene (C_2Cl_4)
RACT — reasonably available control technology
SH — Southern Hemisphere
SIP — State Implementation Plan
SIRA — Stratospheric Impact Research and Assessment
STP — standard temperature and pressure
TCE — trichloroethylene (C_2HCl_3)
TSCA — Toxic Substances Control Act
USDA — United States Department of Agriculture
UV — ultraviolet

UV-A — ultraviolet-A

UV-B — ultraviolet-B

v — volume

VOC — volatile organic chemical

WSU — Washington State University

SYMBOLS

BrO_x — oxides of bromine

$CBrF_3$ — bromotrifluoromethane

$CClF_2CClF_2$ — fluorocarbon-114 (FC-114)

CCl_2FCClF_2 — fluorocarbon-113 (FC-113)

CCl_2F_2 — dichlorodifluoromethane (fluorocarbon-12, FC-12)

CCl_2O — phosgene

CCl_3F — trichlorofluoromethane (fluorocarbon-11, FC-11)

CCl_4 — carbon tetrachloride

CF_3CH_2Cl — fluorocarbon-133 (FC-133)

CF_4 — carbon tetrafluoride (fluorocarbon-14, FC-14)

$CHClF_2$ — chlorodifluoromethane (fluorocarbon-22, FC-22)

$CHCl_3$ — trichloromethane (chloroform)

CHF_3 — trifluoromethane

CH_2BrCH_2Br — ethylene dibromide

CH_2Cl_2 — methylene chloride (dichloromethane)

CH_3Br — methyl bromide

CH_3CClF_2 — fluorocarbon-142A (FC-142A)

CH_3CCl_3 — methyl chloroform (1,1,1-trichloroethane, MCF)

CH_3CHF_2 — fluorocarbon-152A (FC-152A)

CH_3CH_2Cl — ethyl chloride

CH_3COOCH_3 — methyl acetate

CH_3COOH — acetic acid

CH_3Cl — methyl chloride

CH_3I — methyl iodide

CH_3OH — methanol

CH_4 — methane

CO — carbon monoxide

CO_2 — carbon dioxide
CO_x — oxides of carbon
C_2Cl_4 — perchloroethylene (PCE)
C_2HCl_3 — trichloroethylene (TCE)
$C_2HCl_3O_2$ — trichloroacetic acid
C_2H_2 — acetylene
$C_2H_2Cl_2$ — vinylidene chloride
C_2H_6 — ethane
C_3H_4 — methyl acetylene
C_3H_8 — propane
i-C_5H_{12} — neopentane
C_6H_6 — benzene
C_9H_{12} — 1,3,5-trimethylbenzene (1,3,5-$C_6H_3(CH_3)_3$)
$ClCH_2CH_2Cl$ — ethylene dichloride
ClO — chlorine monoxide radical
$ClONO_2$ — chlorine nitrate radical
ClO_x — oxides of chlorine
HBr — hydrogen bromide
HCl — hydrochloric acid; (also) hydrogen chloride
HF — hydrogen fluoride
HNO_3 — nitric acid
$HOCl$ — hypochlorous acid
H_2 — hydrogen gas
NO — nitric oxide
NO_2 — nitrogen dioxide; (also) nitrite radical
NO_x — oxides of nitrogen
N_2O — nitrous oxide
OH — hydroxyl radical
O_3 — ozone
SF_6 — sulfur hexafluoride
SO_2 — sulfur dioxide
τ_ϵ — interhemispheric exchange rate

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EDITOR'S NOTE ON DISCUSSION TRANSCRIPTS

The discussion transcripts included in this volume are based on a verbatim stenographic record of the Conference on Methyl Chloroform and Other Halocarbon Pollutants. Certain editorial changes have been made, however, to correct grammar, increase clarity, and avoid redundancy.

Throughout the transcripts, brackets ([]) indicate parenthetical comments by the editor. The entire document (including discussion transcripts) employs a consistent system of abbreviations and acronyms; individual speakers did not necessarily use these shorthand expressions.

Every effort was made to identify discussion participants, and an alphabetical list of all those so identified is presented as Appendix A. Where there was doubt as to a speaker's identity, the individual has been designated as "Voice from Audience" or with insertion of a question mark after a name.

COMMENTS ON THE LIFETIMES OF ORGANIC MOLECULES IN AIR

A. P. Altshuller

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INTRODUCTION

To begin this paper, a number of actual or potential impacts associated with the more persistent molecules in the atmosphere are innumerated. By "more persistent" are meant those molecules with lifetimes of tenths of a year and longer. Less persistent molecules include those capable of participating in lower tropospheric reactions with nitrogen oxides (NO_x) over hours to days to form ozone (O_3), nitrates, and other products.

Molecules with lifetimes of >1 yr, and especially with lifetimes of >10 yr, can survive long enough to penetrate well into the stratosphere. Therefore, such molecules may participate in the reactions that have been associated with stratospheric O_3 depletion in various models. The accumulation of certain types of more persistent molecules in the stratosphere has also been associated with global-scale climatic impacts.

The more abundant persistent molecules, such as methane (CH_4) and carbon monoxide (CO), participate in determining the distribution of key reactive species, such as the hydroxyl radical (OH), throughout the troposphere and lower stratosphere. In addition, persistent molecules leading to carcinogenic effects or other direct biological impacts contribute to population exposures on all scales from local to global. The total impact of such persistent, biologically-potent species can thus be substantially greater than the impact of molecules with similar potencies but shorter atmospheric lifetimes.

THE TROPOSPHERE AND ORGANIC MOLECULES

The remainder of this paper discusses the tropospheric lifetimes and other tropospheric effects of a variety of molecules, including methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF). Under consideration are certain molecules not presently emitted in significant quantities, as well as other molecules whose emission rates are uncertain or whose atmospheric distributions are not available in any detail. Only a simple approach to computation of tropospheric lifetimes is feasible. Hence the dominant tropospheric removal process is assumed to be OH attack, and an average tropospheric OH concentration of 3.3×10^5 molecules/cm^2 is assumed (Crutzen and Fishman 1977; Fishman and Crutzen 1978). The rate constant expressions for OH reactions with the molecules of interest have been discussed elsewhere (Altshuller 1979). An average tropospheric temperature of 265 K also is assumed. Table 1-1 lists the lifetimes calculated from the expression $t_e = (K\ OH_{avg})^{-1}$.

TABLE 1-1. ESTIMATED LIFETIMES OF METHANE AND HALOGENATED METHANE DERIVATIVES

Compound	Lifetime (yr)	Compound (cont'd.)	Lifetime (yr)
CH_4	29,25,29	CH_3CH_2Cl	0.4[a]
CH_3F	12	CH_3CHF_2	6[a]
CH_3Cl	3.6,4.4	CH_3CHCl_2	0.65[a]
CH_3Br	3.8	CH_3CClF_2	68
CH_2F_2	26	CH_3CCl_3	8,13
CH_2ClF	4.2	CH_2ClCH_2Cl	0.75[a]
CH_2Cl_2	1.4	CH_2BrCH_2Br	0.7[a]
CHF_3	~1000	CF_3CH_2Cl	19[a]
$CHClF_2$	43,41,44	CF_3CHClF	19
$CHCl_2F$	6.2,5.3,6.8	CF_3CHCl_2	4.6
$CHCl_3$	1.5	$CClF_2CH_2Cl$	9.6
C_2H_6	0.6	C_2Cl_4	1.0

[a] Based on rate constants at 265 K estimated by dividing 298 K values by 1.75.

The lifetimes range from 0.4 yr for ethyl chloride (CH_3CH_2Cl) to ~10^3 yr for trifluoromethane (CHF_3). The selection of two available rate constant expressions for MCF resulted in computed lifetimes of 8 and 13 yr. For fluorocarbon-22 (chlorodifluoromethane, $CHClF_2$, FC-22), the three available rate constant expressions lead to K_{265} values quite close to each other so that the computed lifetimes cluster at 41, 43, and 44 yr. Therefore, FC-22 should be substantially more persistent than MCF; with a lifetime in excess of 40 yr, these molecules have ample time to penetrate well into the stratosphere.

A number of the molecules listed in Table 1-1 have been suggested as possible alternative propellants (Midwest Research Institute 1976). One of these molecules is fluorocarbon-142A (CH_3CClF_2, FC-142A), but its computed lifetime of 68 yr may lead to stratospheric damage if it is emitted to the atmosphere in significant quantities. Fluorocarbon-133 (CF_3CH_2Cl, FC-133) has been suggested as an alternative propellant, though it, too, has a relatively long lifetime of 19 yr. But several of the fluorinated molecules do have lifetimes of <10 yr, such as fluorocarbon-152A (CH_3CHF_2, FC-152A), which is also considered a possible alternative propellant (Midwest Research Institute 1976). This compound not only has a shorter lifetime, but would not be expected to participate in the same stratospheric chain reactions as do molecules containing Cl or Br.

The only two brominated compounds in production for which rate constants can be computed with OH are CH_3Br and CH_2BrCH_2Br, which have substantially shorter tropospheric lifetimes than MCF. Both of these molecules also have dispersive emissions that are less than 5 percent of MCF. To contribute to stratospheric O_3 depletion effects, the Br atoms from these molecules would have to participate very effectively alone or in combination with Cl molecules in the reaction sequences of interest.

For several of the molecules listed in Table 1-1, sufficient experimental data are available to permit comparison of computed with measured global concentrations. The computed values are based only on emissions resulting from dispersive losses during manufacturing, storage, or use, because losses from natural sources on land or water, forest fires, and certain other combustion processes lack adequate emission rate estimates.

The atmospheric loading of a substance is computed by adjusting the dispersive losses to the atmosphere for subsequent reactions with OH. These losses are obtained from estimates of the fraction of total production of the substance lost during production, storage, transfer, and use prior to and including 1976. The average rates of consumption of the substance are computed over intervals of lifetimes $t_{0.1}$, $t_{0.2}$, ..., $t_{0.9}$, ..., $t_{0.999}$, and the average rate of consumption for an interval is multiplied by both the length of the interval and the annual dispersive loss estimates related to that interval. To obtain the net mass of the substance remaining in the atmosphere, the net amounts of the substance available after reaction with OH are summed. The mass expressed in grams is converted to milliliters at standard temperature and pressure (STP) and divided by the volume of the earth's atmosphere at STP, resulting in an average global concentration, where a uniform distribution is assumed. In Table 1-2, these computed estimates are compared with average global concentrations obtained experimentally by Singh et al. (1977; 1978; 1979). More details on the dispersive losses and additional experimental measurements available for comparison are given elsewhere (Altshuller 1979).

TABLE 1-2. AVERAGE GLOBAL CONCENTRATION OF HALOCARBONS FROM DISPERSIVE LOSSES

Compound	Net Dispersive Losses (metric tons x 10^{-3})	Average Globa Concentration Obtained Experimentally	Average Global Concentration Computed
CH_3Cl	26	613	3
CH_2Cl_2	491	32	32
$CHCl_3$	24	8	1
$CHClF_2$	270	20-30[a,b]	18
CH_3CCl_3	1667,2025	80[c]	71,86
C_2Cl_4	569	26	20

[a] Midwest Research Institute (1976).
[b] Northern Hemisphere measurement only.
[c] Adjusted to January 1977.

For two of the substances listed, methyl chloride (CH_3Cl) and trichloromethane (chloroform, $CHCl_3$), dispersive losses apparently account for only a small portion of the mass emitted to the atmosphere. While emissions from forest fires and from combustion of chlorinated plastics make contributions, emissions from the oceans appear to be the source for most of the CH_3Cl measured in the atmosphere (Singh et al. 1977; 1978; 1979). The other sources of $CHCl_3$ are not well known. A much lower concentration in the Southern Hemisphere than in the Northern Hemisphere seems to eliminate the oceans as a major source (Singh et al. 1978; 1979). Coastal waters and inland waters are contaminated with $CHCl_3$ that may be formed after chlorination of water, or produced in the bleaching of pulp (Midwest Research Institute 1976). Furthermore, an urban-to-nonurban gradient exists for $CHCl_3$, suggesting one or more sources associated with populated areas.

For the other four compounds considered in Table 1-2 (methylene chloride (dichloromethane, CH_2Cl_2), FC-22, MCF, and perchloroethylene (C_2Cl_4, PCE)), computed and experimental measurements agree reasonably well (Singh et al. 1979), which lends some confidence to the OH concentration utilized. Emission of these four compounds to the atmosphere seems to occur predominantly through dispersive losses in production and storage, and in particular from use as solvents (or, in the case of FC-22, as a refrigerant).

Of the compounds considered in Tables 1-1 and 1-2, at least two — MCF and FC-22 — should be considered as possible contributors to stratospheric O_3 depletion. Because of substantial dispersive losses in the past and projected for the future, and because both compounds have substantial tropospheric lifetimes, the behavior of MCF and FC-22 (especially of MCF in the stratosphere) should be of significant interest and concern. While CH_2Cl_2 and PCE also have substantial dispersive losses to the atmosphere, the shorter lifetimes of these compounds limit their impact on the stratosphere.

The rates of consumption of organic compounds by OH vary widely. As shown in Table 1-3, in terms of time for 1 percent consumption at 40° N latitude in July, the time period involved varies from 23 days for CH_4 to

TABLE 1-3. NUMBER OF DAYS FOR 1 PERCENT CONSUMPTION OF ORGANIC COMPOUNDS BY OH AT 40° N LATITUDE IN JANUARY AND IN JULY

Compound	1% Consumption (days)		Compound	1% Consumption (days)	
	January	July		January	July
CH_4	383	23	C_2H_4	0.18	0.02
C_2H_6	8.2	0.6	$CH_2{=}CHCl$	0.21	0.025
C_3H_8	1.7	0.14	$CHCl{=}CCl_2$	0.6	0.07
$\underline{n}\text{-}C_4H_{10}$	0.8	0.07	$CCl_2{=}CCl_2$	14	1.0
$\underline{i}\text{-}C_4H_{10}$	0.8	0.07	C_3H_6	0.55	0.006
$\underline{i}\text{-}C_5H_{12}$	0.5	0.05			
$C(CH_3)_4$	2.6	0.2	CH_3OH	1.6	0.16
$n\text{-}C_6H_{14}$	0.3	0.03	C_2H_5OH	0.4	0.04
C_6H_{12}	0.23	0.02	C_3H_7OH	0.3	0.03
CH_3Cl	51	3.7	HCHO	0.18	0.02
CH_3Br	55	4.2	CH_3CHO	0.09	0.01
CH_2Cl_2	22	1.5			
$CHCl_3$	23	1.6	CH_3COOCH_3	9	0.9
$CHClF_2$	587	37	$CH_3COOC_2H_5$	0.85	0.08
CH_3CH_2Cl	6.6	0.4	$CH_3COC_2H_5$	0.5	0.05
$ClCH_2CH_2Cl$	11	0.8			
$BrCH_2CH_2Br$	10	0.7	C_6H_6	1.4	0.14
CH_3CCl_3	177	11	$C_6H_5(CH_3)$	0.26	0.025
			$\underline{m}\text{-}C_6H_4(CH_3)_2$	0.07	0.007
C_2H_2	2.7	0.25	$1,3,5\text{-}C_6H_3(CH_3)_3$ or C_9H_{12}	0.025	0.003
C_3H_4	1.7	0.17			

0.003 days for 1,3,5-trimethylbenzene (C_9H_{12}) — a ratio of almost 10000:1. Comparison of the January rate of CH_4 consumption with the July rate of C_9H_{12} consumption increases this ratio to over 100000:1. Finally, if the rate of CH_4 consumption in January at 55° N latitude is compared with the rate of C_9H_{12} consumption in July at 25° N latitude, the ratio increases to over 1000000:1. Because the ratio of OH concentrations at 25° N to 55° N latitude is 3:1 in July, but 60:1 in January (Crutzen and Fishman 1977; Fishman and Crutzen 1978), winter season differences in rates of consumption of organic molecules are especially significant as a function of latitude. These conditions indicate consideration of not only the intrinsic differences in reactivity of organic compounds, but also of latitude and season of occurrence, if transformations of these substances on regional or continental scales of movement are at issue.

Most organic compounds listed in Table 1-3 have previously been demonstrated to undergo reactions with NO_x in sunlight, forming significant levels of O_3 and consuming substantial amounts of the organics. These reactions occur within the first 24 hours after emission to the atmosphere under summertime conditions (Altshuller 1977). Of importance is that the more reactive of these organic compounds have rates of consumption by OH differing by less than a factor of 100 for a given season and latitude (Table 1-3). For example, in July at 40° N latitude, the times for 1 percent consumption which are from 2 to 25 times longer than for C_9H_{12} include all of the alkanes larger than propane (C_3H_8), all of the alkenes except PCE, all of the alcohols except methanol (CH_3OH), all of the esters except methyl acetate (CH_3COOCH_3), and all of the listed aromatic hydrocarbons except benzene (C_6H_6). Therefore, though a substantial number of very persistent halogenated alkanes exists, the number of hydrocarbons in other series which are persistent is rather small during the summer months.

A question of considerable interest relates to determining which persistent organic substances undergo very slow reactions with NO_x, thereby producing insignificant amounts of O_3 in the lower troposphere. While the boundary area of such reactions cannot be defined in absolute terms from the discussion above, the importance of latitude and season of the year on reactivity in these systems should be clear. Since the homogeneous oxidations of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are dominated by reaction with OH radicals, these reactions also will show strong dependencies on latitude and season of the year.

Although most of the organic compounds listed in Table 1-3 disappear rapidly in terms of hemispheric transport times, their consumption can be slow compared to their movements on a regional or continental scale. In January, all except the most reactive compounds undergo much less than 50 percent conversion within a week's time at a latitude of 40° N or above. In July, such organic compounds as ethane (C_2H_6), C_3H_8, neopentane ($\underline{i}$-C_5H_{12}), halogenated alkanes, acetylene (C_2H_2), methyl acetylene (C_3H_4), CH_3OH, and C_6H_6 undergo conversion by OH of 50 percent or less during a 1-week period at 40° N latitude or above.

Air parcels moving in trajectories over the North American continent usually traverse most of the continent within a week. Because such movements are rapid in comparison to July conversion of the more persistent organic compounds and to conversion of most organic compounds in winter, rural and even "remote" continental sites may be fumigated by air parcels containing such compounds from urban centers and industrialized areas. Therefore, measurements at these sites are not necessarily useful in providing tropospheric background levels or in providing uncontaminated samples of natural organic compounds.

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DISCUSSION

Dr. Jesson: A point of information: The lifetime you showed on the slide [Table 1-1] seemed relatively long. What was the average?

Dr. Altshuller: 3×10^5, a value which will raise considerable discussion. This value comes out of the Crutzen and Fishman model, is derived from Singh's computations, and is in fairly good agreement with the experimental measurements by Campbell et al. With much higher OH concentrations, at least according to these calculations, tropospheric concentrations of these molecules occur that are extremely small, in comparison with experimental concentrations. So one must rationalize these discrepancies when using the values. I'm not arguing the point between 3 and 4×10^{-5}. At 10^6, 2×10^6, and so forth, however, it appears one must take into account other chemical reactions and kinetics in terms of rationalizing the lifetimes of quite a few molecules.

Dr. Riordan: Your one box model: Does that require reproduction? And where did you get that term?

Dr. Altshuller: Yes, for the values I cited from the missing slide [Table 1-2], it indeed does. Of course, MCF values have been discussed in some detail. Molecules of a relatively short lifetime present no great problem, because the time period that must be considered in the calculations extends back only a few years from the point when emission is assumed. That is the cutoff point for molecules like PCE or CH_2Cl_2, for example. The molecules emitted 5 or 10 yr earlier make no contribution because they consume. So only a short historical record backwards is needed to use such information as the A. D. Little data on production and usage pattern and losses from the usage patterns for these individual molecules. In some cases, however, difficulties can arise; for example, although U.S. production losses can be rather well estimated, global production and losses cannot be accurately estimated using only the A. D. Little data.

STATUS OF THE
STRATOSPHERIC OZONE DEPLETION ISSUE, INCLUDING COMMENTS ON METHYL CHLOROFORM

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EDITOR'S NOTE: Because Dr. Rowland did not provide a formal manuscript for publication in this volume, the stenographic transcript of his presentation has been edited and reproduced below.

PRESENTATION

In going over and preparing a discussion of the status of the stratospheric ozone (O_3) issue, I decided that it would be worthwhile to start at the beginning and review what we know (or what there is reasonable agreement about) as well as the areas of disagreement. I'm going to do this mostly from slides.

This is a reproduction of the data of Lovelock taken in late 1971 and published in 1973, showing the amount of fluorocarbon-11 (trichlorofluoromethane, CCl_3F, FC-11) measured in the air as a function of latitude. This, then, is the first measured set of data for FC-11. It is, basically, the starting point of concern about halocarbons in the atmosphere. If you want to check the range, it goes from 80 ppt to 40 ppt (these are 1971 levels). The first question, I think, raised about such molecules measured in the troposphere was whether or not they reach the stratosphere. I think it is worth reminding people that this question was raised and is now effectively settled.

This shows the prediction, in 1974, of dependence of fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2, FC-12). In this case, it is concentration as a function of altitude. If we go to the top of the troposphere, we would expect to see a decreasing amount as altitude increases into the stratosphere. That was one of the first aspects that needed to be tested, and it has now been tested. The next two slides show one of the mechanisms for doing that.

These are the grab sample flasks of the National Oceanic and Atmospheric Administration (NOAA). The next slide shows them going up with the instrument package. The next slide shows the measurements that were made in that way.

The NOAA samples are shown here, along with the National Center for Atmospheric Research (NCAR) samples. These are the measurements of 1975. The measurements, of course, have been repeated very many times since then. Measurements are now available for the tropics and for high-latitude regions.

This slide was calculated for 30° latitude. Measurements were near that. The tropic line, of course, shows a higher level, and high-altitude levels would be below this. But what one finds, basically, is that the fluorocarbons do reach the stratosphere and do fall off in altitude, as would be expected with an effective stratospheric photodissociation process. If decomposition did not occur, levels would go off much more towards these values. Thus, the line here shows not only penetration to the stratosphere but also decomposition of the molecules themselves.

In the original inquiries into what would happen after the molecules reached the stratosphere, investigators tried to identify the chlorinated species that would be expected. The first expected chlorinated species to be identified was the Cl atom, which is released by photolysis of the chlorinated molecule. Starting with the Cl atom, investigators have had to include all possible reactions that might occur in the stratosphere by taking into account the various species existing there. Of course, it is possible to compile a list of 20 or 30 or more chlorinated species. The question is: "How many of these play an appreciable role in the atmosphere?" In our original list, we showed Cl and the chlorine monoxide radical (ClO), involving the reactions shown here. If you want to arrive at a calculated distribution of these within the stratosphere, then you need the right constants for all the reactions involved. For example, for OH + HCl you need the right constant in that atmospheric temperature. You need to know the photolysis rates involved. During the last several years, then, essentially all the reaction rates shown here were measured in the laboratory to sufficient accuracies that large errors remaining in any of these processes is unlikely.

The remaining question, then, is: "Are all of the molecules included?" Obviously, this is the original version of the slide: it does not have the chlorine nitrate radical ($ClONO_2$). My present feeling is that it is almost time to take $ClONO_2$ back out again, in terms of being important. Nevertheless, one can calculate that there should be some $ClONO_2$ present. I think the present uncertainty about this formation rate results from the fact that most of the methods for measuring the rate of disappearance of ClO in the presence of the nitrite radical (NO_2) did not establish this as the product. That is probably not a trivial exception to raise at this point. It is quite possible that ClO, in combining with NO_2, can make molecules other than $ClONO_2$. It may hook on in a different way, so that it becomes ClOONO (or something of this sort). Also, there are some indications at the present time (e.g., Knauss in Germany and Molina of the University of California) that this rate of formation is slower than the rate used in the National Academy of Sciences (NAS) calculation. If the rate of formation is slower, it will have considerable effect. Probably the area in which it will make the biggest difference is rate of removal of ClO after sunset. For comparison with nighttime measurements, we need to know this rate fairly accurately, because it tells us how quickly ClO falls off once the sun goes down. So the question, here, concerns ClO + NO_2: What is the product, and how well is it known? The values for this rate that are being used are upper limits, I believe. The photolysis rate, I believe, is reasonably well known at the present time.

Other molecules have been suggested here. Hypochlorous acid (HOCl), for example, is a molecule which from time to time has been suggested as important. That depends on the rate of photolysis of HOCl. The present situation, I believe, is that the absorption cross sections of HOCl have been shown to be sufficiently large in the region between 3000 and 4000 Å. Thus, HOCl does not have a long time in the stratosphere and cannot build up to be an important compound. You can still write formation reactions for it with ClO and HO_2. But it will also have a rapid removal process, and seems not to affect the overall calculation in any way.

This does illustrate that you can go through and look for other processes. If you ask "What is important?," the question becomes "How small a concentration are you concerned about?" That, in turn, probably depends on whether there are any catalytic processes involving the particular molecule or whether there is any way of stopping other catalytic processes. I believe that there is reasonable agreement, at the present time, on the set of compounds shown here.

The next slide simply illustrates the progress of the measurements. These are Julius Chang's calculations of a year and a half ago, showing a distribution including a Cl atom here, this amount of ClO, a fairly substantial amount of $ClONO_2$, and HCl as the predominant molecule.

It is necessary, next, to perform stratospheric measurements to confirm or deny the existence of these various compounds in the concentrations indicated here, or in relative concentrations. The next slides illustrate one of the methods of doing that.

This was taken from the work of Dave Murcray. It involves infrared (IR) spectra taken at an altitude of 30 km (typically, looking at the setting sun: sunset = 90°). This is the zenith angle of the sun and this is 5° below the horizon. It's below the horizon at ground level but still barely visible for below the 30 km. We have long pathlengths through the atmosphere, here. We see carbon dioxide (CO_2) throughout. Here is FC-11 (the broad adsorption peak under there). Here is FC-12. Nitric acid (HNO_3) is only in the stratosphere; water vapor is only in the troposphere. The existence of such measurements makes it possible, then, to go back and look in older spectra, or to continue to look in new spectra, for other molecules such as $ClONO_2$. Current measurements of $ClONO_2$, as I understand them, simply provide an upper limit. The apparent broadening of an O_3 peak, if you attribute it to absorption by $ClONO_2$, is then more or less in agreement with the upper limits of the calculations. Thus, it looks as though there might be some $ClONO_2$ there. But it is certainly not cleanly identified as $ClONO_2$, and it is certainly not present in large quantities.

This slide shows the measurement. This is Jim Anderson's resonance fluorescent apparatus in flight. This is an earlier version of the present apparatus, which has four pods that measure simultaneously and can measure Cl, ClO, NO_2, and so forth.

This slide illustrates the first (prepublished) runs of Jim Anderson in which ClO was detected in the atmosphere. Detection of the Cl atom was direct. ClO was detected indirectly, following conversion of ClO to carbon monoxide (CO) by reaction with nitric oxide (NO) in the apparatus. According to my most recent conversation with Anderson, he has had 10 good measurements analyzed, 9 of which are in reasonable agreement. The basic situation is that there is a spread in his values. There is one high outlier that is very difficult to explain by any process, other than to say that something is experimentally wrong on the particular flight. If there is something experimentally wrong on a particular flight, then we should perhaps raise the question of whether the error was present in the other 9 flights, as well. So, we must really work hard to understand that high outlier. There are some very low probability events that might be a source of Cl for a particular case. I think we should watch Anderson's results and see if he gets more high outliers or if it turns out to be just one run which is not reproduced at any later time.

There are other measurements of ClO, including the very recent heterodyne measurements by the Jet Propulsion Laboratory (JPL), which give a somewhat different profile up here. The microwave measurements of ClO (also by JPL) are in agreement not with the Anderson high outlier but with the general bulk of measurements (which are down low). The Cl:ClO ratio seems to be in good order in these experiments (probably within a factor of 2). Whether we should do better than that is a question that can still be asked. In general, I think we can say that several techniques have seen ClO in semiquantitative agreement with the expectation of the calculations.

There is a measurement of the Cl atom. This concentration is much lower, so it's a harder measurement to do. The Cl chemistry looks consistent, with the exception of the high value that Anderson obtained on one flight.

As for production of FC-11 and FC-12 over the most recent years, we can see how the FC-11 concentration would have settled here and then more or less flattened out. I don't know whether this is going to show any more downward change. It is certainly a very slow change from the peak. Certainly, from 1972 and 1973, there hasn't been much change. Essentially, then, in the early 1970's we moved into a steady-state period in which production is reasonably constant. This happens to match nearly all calculations in which everything is held constant starting at a particular point. What it suggests to me is that regulatory actions taken so far have had very little effect. The amount of production is essentially the same as before. U.S. regulatory actions for aerosols, or the fact that they were coming into effect, did certainly affect use of FC-11 and FC-12 as aerosol propellants. But they did not appreciably affect total worldwide use. This is due partly to diversion of FC-11 and FC-12 into other uses in the U.S. and to increased usage outside the country, where no regulatory actions have been taken. The last time I referred to the Chemical Marketing Reporter in regard to carbon tetrachloride (CCl_4) (the precursor to FC-11 and FC-12), the journal's assessment was that the decrease in CCl_4 production reflecting regulatory action had already essentially occurred, and that production would start to rise again. And the journal was optimistic for increased production in 1980. I'm not sure of the basis for that optimism.

A major, further question in terms of FC-11 and FC-12 is that of tropospheric sinks. The subject has been raised for the last four or five years, and a whole set of different possible reactions has been suggested. The problem is to find a tropospheric sink of appreciable importance. For example, destruction in the internal combustion engine of the American automobile will remove all FC-11 and FC-12 within 100000 yr. That is certainly a sink, but it's not an important sink. So far, no one has been able to identify a particular sink which, by itself, is important. That leaves the alternative of trying to find an undiscovered sink or accumulation of undiscovered sinks that could be important. One of the methods of doing that is to simply calculate how much FC-11 or FC-12 should be present and to compare it with the amount observed to be present.

The next slide reproduces Lovelock's measurements again. Up here, going even higher and higher, are the measurements made by Makide in my laboratory about a year ago. Makide's values are not appreciably different from Singh's. This is FC-11. Basically, between the Northern Hemisphere (NH) and Southern Hemisphere (SH) there is very little gradient. At this point, it was ~150; here, ~130. This is a gradient between the NH and SH on the order of only 10 percent. Contrast that with the gradient of Lovelock: an enormous gradient in the NH itself, and also a gradient between the NH and SH. Now, if we're going to make a comparison calculation of the amount of fluorocarbon in the atmosphere, it is important to know how to weight these various amounts. If the concentration doesn't change a great deal, it doesn't make too much difference. But if there's a big change (such as Lovelock's values indicate), weighting the SH relative to measurements made in the north temperate region will underestimate the amount of material in the SH.

One thing that is obvious right from the beginning is that the amount in the atmosphere has gone up by a factor of ~2 since the first measurements were made. Thus, FC-11 and FC-12 are certainly accumulating in the atmosphere at a rate at which — in 6 or 7 yr — they have approximately doubled. That is in agreement with the amount of FC-11 that has been released to the atmosphere in a semiquantitative fashion.

The next slide shows a comparison of these different weighting measurements. A couple of research groups, including the du Pont research group, have mentioned tropospheric sinks of lifetimes of 10 to 20 yr. They have weighted their data using a reproduction, basically, of Lovelock's values.

The calculation on which Molina and I collaborated a couple of years ago assumed reasonably rapid mixing between the NH and SH which would take ~2 yr.

This gave us a value of ~80 percent as much in the SH as in the NH. In contrast, the other weighting shown here is on the order of 60 percent as much. You can see the difference between these two weightings; there's a substantial amount of material in between. The crosshatched area shows the amount our measurement would have to be reduced to get a 20-yr tropospheric lifetime. This indicates several things. First, it is important how you weight. Also, it's going to be difficult to make very accurate measurements. To begin to eliminate tropospheric lifetimes on the order of 40 to 50 yr would require very, very accurate measurements. Experimentally, that would be an almost impossible task, I think.

The next slide shows the same data and compares the first results obtained here. This is as of a couple of years ago; since that time, the data have tended to be a little bit higher, I believe. This shows that we also underestimated the SH, but not by as much as the du Pont group did. Of course, the NH and tropic region were also grossly underestimated in those. When we do the same calculation over again now (take our own data and weight them), the measurements are made from 55° N to 55° S. So we're not having to extrapolate long distances. In fact, the calculations show that there is reasonably uniform mixing (say, 10 percent) and not much of a gradient. When we calculate the amount that is present, we again come out with a finding for FC-11 that is in reasonable agreement with the amount expected to be in the atmosphere after correcting for stratospheric loss, with no indication of any appreciable tropospheric sink. We obtain the same result for FC-12. Actually, as far as we're concerned there seems to be a little bit of a discrepancy in the other direction. We seem to find a little bit more than we might expect, underestimating stratospheric loss. But that is probably within error of the measurement.

In summary, our measurements so far indicate no need to introduce any process except stratospheric loss to account for removal of FC-11 and FC-12. We can then go into a calculation of what this means in terms of O_3 depletion.

Shown here is the growth with time. This is the NAS curve as calculated by Julius Chang. This is the calculation of 1977, with the first revision of

HO_2 + NO rate and going to -15 percent. The most recent number, I believe, is 18.6 percent. The basic change has been HO_2 + NO. This rate constant, being very much faster, makes NO_x in the lower stratosphere no longer an O_3 depleter, to put it crudely. Tying it up with $ClONO_2$ doesn't have any effect on the Cl calculation. As a result, the effect of Cl went up by a factor of 2 or, perhaps, somewhat more than the most recent calculations.

At the present time, then, I think the calculations are suggesting numbers in the 15 to 20 percent region. That is what we would expect for steady-state depletion with continued release of FC-11 and FC-12 at the rates that have been common all through the mid-1970's. I think it is worth pointing out, too, that it's easy to calculate but it is easy to be misstated. When one says that the calculation is "15 percent," that's the asymptotic value that one is looking for. Of course, you can reach the asymptote any time you want — the year 2500 or the year 3000.

I think it's probably worthwhile to start talking about the depletions expected at particular time periods. The current estimate would be a depletion on the order of 2 percent. Well, if you look at these numbers coming out to the year 2000, you're ~1/3 of the way to the asymptote; out to ~2035, you're ~2/3 of the way to the asymptote. So you get ~1/3 of the result by the end of this centry and ~2/3 of the result 1/3 of the way through the next century. Whatever value you're going through here, keep in mind that you get 1/3 of it. A value of 20 percent means 67 percent by the end of this century. And 14 percent, say, by the year 2035. That gives you some idea of the time scale on which this would develop.

These are ultraviolet (UV) measurements taken in 1974 at Mauna Loa, Hawaii and Bismarck, North Dakota with a device that measures the amount of UV in the sun received by the device from January to January. As you can see, the amount of UV radiation received in the northern tier of the U.S. is not much less in mid-summer than it is in Mauna Loa. Of course, there's a lot more radiation received over the whole year there. If we know that Mauna Loa is at 19° and Bismarck is at 6°, we can integrate under this to see what the total UV exposure would be here. You can't move too easily from that to knowing what the exposure would be for human beings, because you have to know what fraction of time they spend in the sun all through these periods. But the correlation certainly is that more UV-B is available the closer you get to the equator.

This is a typical curve of the incidence of skin cancer as a function of latitude. Measurements were made at 10 different stations. Looking at the correlation, there are three things that come in: cloud cover, altitude, and latitude. These take care of almost all of the risks of the variations involved. There's very little altitude effect; ~70 percent of the effect is latitude.

Curves of this sort show a higher incidence of skin cancer in the southern as opposed to northern U.S. Coupled with the curves I've shown before, this leads to calculations of predicted increases in human skin cancer as a result of depletions in O_3.

If you accrued the figure — if you were to deplete the O_3 by 10 percent — you would get a 20 percent increase in UV-B (the sunburn ultraviolet). And that would lead to a 30 percent increase in human skin cancer. The accuracy of those numbers is not great, because it involves taking slopes of this kind and making assumptions about human exposures.

The cancer is malignant melanoma. The O_3 measurements were taken at Arosa in Switzerland, and the data are plotted in two ways. One plot, the blue lines, shows yearly values over the 50-yr period. The red line shows the 5-yr running average. The 5-yr running average, as you can see, ends in 1975. The blue lines come back up again. The 5-yr running average is still down. At the end of 1977, the 5-yr running average was at its lowest point since the start of measurements.

There are two things that we can see here: First, there is enormous fluctuation. Also, the change is 5 percent in one direction or the other. An actual O_3 gain or loss on top of that fluctuated pattern would probably mean a change of several percent. If we had comparable data from large numbers of stations going back over 50 yr, then we could cut down on that. But such data and stations simply don't exist. Many of the stations which do exist have calibration problems that are generally absent from these Arosa data. This has been a major project over a long period of time, and they have done a lot in terms of calibrating their apparatus on a regular basis and trying to take out all the instrumental variations that you get in a 50-yr time sequence of this sort. There is certainly a question as to how much O_3 change we would have to see in order to demonstrate a loss of O_3. It still looks to me as though several percent would be required. And even though this 5-yr running average is down at a low point, we cannot conclude one way or the other whether it is on a general downward trend or will come back up in the future.

The next slide brings in methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF). I will just briefly describe what we have done here. First, MCF certainly has a tropospheric sink. There's a known tropospheric sink in the reaction of the hydroxyl radical (OH). The question of how much OH is actually present on a world-wide average is still open, and the MCF residence time has been estimated at anywhere from ~1 to ~15 yr. Of course, that makes an enormous difference as far as possible regulatory action might be concerned. It also makes a big difference because MCF offers a good chance to calibrate the effect we would expect for other CH-containing compounds, such as some that Dr. Altshuller mentioned earlier. It's important to get a good measurement of the lifetime of MCF.

My group (like several others) has tried to do that. We've made the latitude measurement shown here. Basically, these measurements were made in the vicinity of January 1978 and have been corrected to January 1, 1978. The measurements were all made within 1.5 months on either side of that date and were corrected on the basis of a 1 percent/month change.

Now, MCF is going up rapidly. So we need to know exactly what date we're talking about when we discuss concentrations. Shown here are the NH and SH temperate zones. There are only a few tropic measurements. What we have done is to interpret the worldwide average as of January 1, which was 80 ppt. The question of the NH average depends somewhat on what is done in the tropics.

Here there is only one measurement. All of these measurements, with the exception of this one, were made on ocean coastlines where the prevailing wind was off the ocean. So these are Alaska, the West Coast, the West Indies, and Chile.

There are two things that we can do here. One, we can take the whole 80 ppt worldwide average, compare it with the calculated emissions given by Dow, and see what that gives us for the lifetime on a worldwide basis. We can also interpret it in terms of the N/S ratio. For that, we need to make some assumption about the relative concentrations of OH in the two hemispheres. This last slide shows a calculation of that. Here is our N/S ratio. As you can see, we arrive at a lifetime on the order of 6 yr. Looking at these cross-hatched lines, the main thing is that the 0.15 lines cross here, not far from the measured point. The fact that the calculated rates of removal in the NH and SH are about the same makes it difficult to accommodate large excesses of OH in the SH. That is, at this point, we should have much less in the SH. We have a different N/S ratio coming down here. If removal were twice as fast in the SH, we would expect it to be somwhere down here. And we just don't see that. So, as far as MCF is concerned, we're using 15 months as the exchange time between the two hemispheres. It looks to us as though the OH rate of removal is about the same in the two hemispheres, and that the lifetime of MCF is ~6 yr, which is somewhat less than the value Dr. Altshuller calculated.

We've done the same thing with methane (CH_4). The lifetime of CH_4 ought to be 2 to 2.5 times longer. Dr. Altshuller's calculated value was 25 or 30 yr. It's very hard (if not impossible) to explain a 25- to 30-yr lifetime for CH_4 on the basis of OH removal. Also, there is a gradient in the troposphere. There is 7 percent more CH_4 in the north temperate region than in the south temperate region. If there's more CH_4 in the NH, you expect it, I think, to be produced there, because that's where the landmass is. Nevertheless, it's very difficult to accommodate anything more than ~12 yr for the lifetime of CH_4. And that forces the MCF lifetime down to 5 or 6 yr, in order to get a gradient.

DISCUSSION

Voice from Audience: In your calculation, you showed the photodissociation of $ClONO_2$. I think the group would suggest that —

Dr. Rowland: Regarding the photolysis product of $ClONO_2$, there's a publication by Smith[8] and me in which ClONO + O is shown to form. That photolysis was at 3025 Å. In order to calculate what happens next, the ensuing behavior of ClONO must be known, and that turns out to be essentially a null process. The measurements by Golden's group were at 2700 Å, and those measurements may not be pertinent to what happens at 3100 Å. They are flashing, actually, so they have much more energy available.

If Cl atoms were present in our system, then adding CH_4 — which we tried — should take them out. We did not find HCl. So, under our conditions, we concluded that Cl atoms were not present. If you accept Cl + NO_3, your calculation then depends on whether NO_3 becomes NO + NO_2 or NO_2 + O. It can cause further O_3 depletion under some circumstances, but I don't think it's a big effect. And I'm not sure that their [Golden group] results are pertinent for the wavelengths that are important in stratospheric photolysis.

Voice from Audience: In the two checks of the tropospheric lifetime of MCF, the overall average depends clearly on efficient figures and absolute accuracy of the measurements. Could you say a few words on the accuracy of your figures? Perhaps we should ask a few other people, too.

Dr. Rowland: We think they're good to ±6 ppt — 80 ±6 ppt. We think our numbers are in disagreement with Dr. Singh's numbers.

Dr. Rasmussen: We have integrated average values for FC-12, FC-11, MCF, and CCl_4 based upon ~1000 measurements since 1976. All data represent grab samples or traveling samples obtained on aircraft flights, or surface measurements at various locations. The important point is the integrated averages are weighted for the latitudinal atmospheric mass ratio.

As Dr. Rowland stated, his 13 points gave an interhemispheric average for MCF with a difference of ~1.29. Our values resulted in ~1.26 for 1978. However, in 1979 a very interesting anomaly was observed that was not attributable to calibration; in these data sets, we have maintained the same primary calibration standards since 1976. In any case, no real difference is seen between Rowland's MCF data and our own, in view of the relative difference between hemispheres and based on a global average. The absolute numbers may differ, likely because of a ~20 percent systematic difference.

Dr. Rowland: A 20 percent difference in measurements of the absolute concentrations means a factor of ~1.6 in the lifetime of MCF. For many purposes, a factor of 1.6 is not very important at all. Whether 6, 9, or 10 yr is calculated for the tropospheric lifetime, the qualitative and the semiquantitative conclusions are basically unaffected: MCF remains in the troposphere long enough for some of it to enter the stratosphere. We're not talking about big differences, in any event, between Singh's or Rasmussen's and our values, but a relatively small difference of ~20 percent.

Voice from Audience: Is the MCF and OH reaction product trichloroethylene or -ethene?

Dr. Rowland: I purposely wrote it as $C_2Cl_3H_2$ to not indicate where the chlorines were.

Voice from Audience: I am perhaps showing my ignorance. But if it's an ethane, wouldn't there be another hydrogen? Wouldn't there be one less?

Dr. Rowland: That would result in a trichloroethyl radical.

Voice from Audience: What is the half-life of that radical? Isn't that an important consideration here, taking it all the way down to HCl?

Dr. Rowland: It's important but it's not clearly understood; I write it this way because a one, two atom shift is suspected to occur immediately after the abstraction process. Demonstrating the nature of this trichloroethyl radical and its reaction products is something we're working on in the laboratory. Certainly no statement in the literature describes the processes exactly. The overall assumption, however, is that — unless some molecule is found to be stable against photolysis — all three chlorines will be released. This must be demonstrated. Arguments can be made that certainly one and maybe two of them are given off, but the exact pathways are not known.

Voice from Audience: Are you implying that with this radical, at least for two chlorines, that the effect on O_3 depletion could be substantially beyond what we are estimating at this point?

Dr. Rowland: With a lifetime in the 6- to 10-yr range, about 15 to 20 percent of the MCF will be decomposed in the stratosphere; and the first-order approximation is for all chlorines to be released. Therefore, a stratospheric Cl source would be available from the decomposition of MCF. The effect of fluorocarbons would decrease by roughly the fraction destroyed in the stratosphere, which, as I say, is 15 to 20 percent. On a tonnage basis, the fluorocarbon problem is 1/5 to 1/10.

ENVIRONMENTAL FATE OF METHYL CHLOROFORM

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INTRODUCTION

In order to study the environmental fate of a chemical, two vital processes must be considered: transport and transformation. Once adequate knowledge is available in these areas, an assessment can be made of the concentration that will produce an impact on the various ecosystems.

Transport deals with movement of the material within and between major environmental compartments. In the case of a volatile chemical, the compartments of main concern are the troposphere, stratosphere, and hydrosphere. The lithosphere, composing only 30 percent of the earth's surface, will be neglected for the low-molecular-weight halocarbons that are the subject of this report.

Transformation concerns the chemical reactions affecting a substance emitted to the atmosphere. These reactions are important for cleansing the system of the chemical. With continued addition of a product in the absence of dissipating mechanisms, the load, and hence the concentration, build to an undesirable level at a future point in time. The precise time is dictated by the rate at which the agent is added and by its intrinsic toxicity or other adverse effect.

The bottom line in studying environmental fate is to ascertain the potential impact on the earth's biosphere. The impact may be either direct or indirect. A direct effect would be a chemical buildup that becomes toxic to susceptible organisms. An indirect effect might be expressed through a series of reactions that results in an undesirable biological event.

Fluorocarbon-11 (trichlorofluoromethane, CCl_3F, FC-11) and fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2, FC-12) have become classic examples of compounds thought to produce such an indirect effect. Molina and Rowland (1974a) observed that no known dissipating reactions occur for these volatile chlorofluoromethanes (CFM's) in the lower atmosphere, which led them to the stratosphere. In investigating the degradation of CFM's in the stratosphere, they became aware of the possible impact of the reactions on depletion of the ozone (O_3) layer. The proposed biological consequences of this depletion have since led to legislation and regulations controlling emissions of these compounds.

Through the same line of investigative reasoning, methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF) has become involved in a somewhat similar environmental issue (McConnell and Schiff 1978; Singh 1977; Crutzen et al. 1978). Resolution of this issue is the crux of the present workshop.

This report considers two major questions:

(1) What is the residence time of MCF in the troposphere? This length of time is critical, since it indicates how much of the released chemical will reach the stratosphere intact. Numbers of years ranging from 1 (Chang and Wuebbles 1976) to 8 (Singh 1977) have been suggested.

In order to avoid any confusion, the relation between rate constant, residence time, and half-life should be mentioned. These are all related by Equations 1 and 2. The half-life

$$t_{1/2} = \ln 2/k \qquad \text{(Eq. 1)}$$

where k = first-order rate constant in reciprocal time units is the time required to reduce the concentration by one-half. The residence time

$$\text{residence time} = 1/k \qquad \text{(Eq. 2)}$$

is the average length of time that a chemical will remain in an environmental compartment under a reaction subjected to the rate constant, k.

(2) What is the impact of MCF on the stratospheric O_3 layer? Presentation of a few major unresolved questions will illustrate the uncertainty regarding halocarbon impact on this important gaseous layer.

RESIDENCE TIME OF METHYL CHLOROFORM IN THE TROPOSPHERE

Stochastic Approach

In this approach, the historical emission of MCF is statistically fit to monitoring data collected on MCF in the troposphere. The model to be used is shown in Figure 3-1 and has been reported previously (Neely 1977; Neely and Plonka 1978). The first task is to establish meaningful values for the rate constants in Figure 3-1:

(1) The input for the model is shown in Table 3-1 and is the Dow Chemical Company's best estimate of the worldwide emission of this solvent to the troposphere. Since the Southern Hemisphere (SH) can be emitting no more than 3 percent of the total (according to our estimate of the use pattern), the material is assumed to be vented in the Northern Hemisphere (NH).

The input (k_o) is expressed as a continuous function of time by linear interpolation between the annual emission rates shown in Table 3-1.

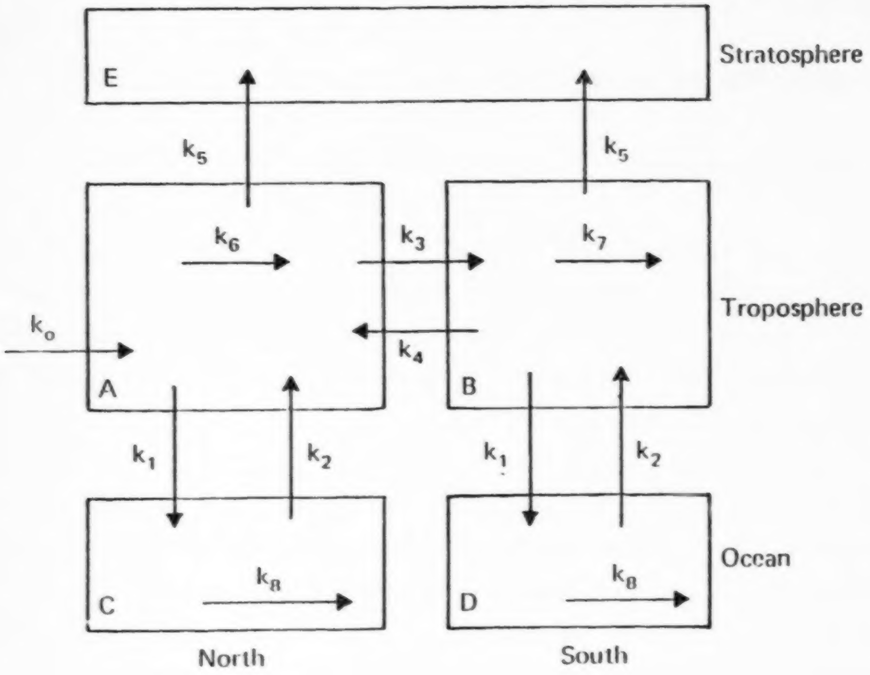
E
Stratosphere
k_5
k_5
k_6
k_3
k_7
Troposphere
k_o
k_4
A
B
k_1
k_2
k_1
k_2
Ocean
k_8
k_8
C
D
North
South

Figure 3-1. Statistical model used to fit monitoring data collected on MCF in the troposphere. Statistical determination of rate constants k_6 and k_7 is given in Table 3-4.

TABLE 3-1. WORLDWIDE GLOBAL EMISSION OF METHYL CHLOROFORM

Year	Released to Atmosphere (millions of pounds)	Percent Change
1951	0.3	
1952	0.5	66.6
1953	2.1	320
1954	6.0	185
1955	17.6	193
1956	27.4	56
1957	43.2	57
1958	45.7	5.7
1959	66.8	46
1960	79.6	19.16
1961	83.8	5.2
1962	124	48
1963	112	-9.6
1964	125	11
1965	161	28
1966	240	49
1967	288	20
1968	320	11
1969	327	2.19
1970	341	4.28
1971	368	7.9
1972	508	38
1973	750	47.6
1974	800	6.67
1975	804	0.5
1976	917	14.05
1977	940	6.87
1978	1050	12.2
Total	8548	

(2) The interhemispheric exchange constants (k_3 and k_4) are assigned values ranging from 1 to 0.70/yr, based on previous studies (Singh 1977; Pressman and Warneck 1970). A range of 0.71 to 0.86/yr, representing a residence time of 14 to 17 months, is used in this study.

(3) The estimated exchange rate between the oceans and the atmosphere is based on the studies of Liss and Slater (1974), McKay and Leinonen (1975), and Neely (1976). Using a mixing depth of 10 km in the troposphere and 100 m in the ocean (Neely and Plonka 1978), values for k_1 and k_2 are calculated (see Table 3-2).

(4) Rate constants for MCF movement from the troposphere to the stratosphere are assigned values ranging from 0.02 to 0.03/yr, as suggested by earlier CFM work (Neely 1977).

Using these rate constants and the values of the parameters shown in Table 3-2, a statistical fit is made to the data shown in Table 3-3. An average value of 1.49 for the North/South ratio is used to estimate the SH concentration. The two parameters adjusted are the dissipating rate constants k_6 and k_7. These results are summarized in Table 3-4.

TABLE 3-2. PARAMETERS FOR THE STATISTICAL MODEL SHOWN IN FIGURE 3-1[a]

Parameters	Description	Value
V_1, V_2	Weight of air in 1/2 of troposphere assuming height of 10 km	2×10^{21} g
V_3	Weight of water in NH	1.54×10^{22} g
V_4	Weight of water in SH	2.09×10^{22} g
k_1	Flux between air and ocean	9.98/yr
k_2	Flux between water and air	0.066/yr
k_5	Transfer from troposphere to stratosphere	0.02 - 0.03/yr
k_3, k_4	Transfer between NH and SH	0.86 - 0.71/yr

[a] Taken from Neely and Plonka (1978).

TABLE 3-3. MONITORING DATA ON METHYL CHLOROFORM IN THE NORTHERN TROPOSPHERE

Year	Concentration (ppt)		North/South Ratio	Reference
1972.0	37	(24-45)[a]		Lovelock (1977)
1973.5	52.5	(42-60)		Lovelock (1977)
1974.4	68	(60-76)		Lovelock (1977)
1975.5	80	(75-85)		Lovelock (1977)
1976.3	85	(80-90)		Lovelock (1977)
1976.5	92	(88-95)	1.51	Lovelock (1977)
1976.3	85	(70-92)	1.47	Rasmussen et al. (1976)
1978.0	98		1.49	Rowland (preliminary data)

[a] Estimated range.

Table 3-4 indicates that a 20 percent increase in k_3 and k_4 causes a 30 percent decrease in k_6 and a 44 percent increase in k_7. The overall effect changes neither the average dissipation rate constant nor the calculated tropospheric concentrations, but does alter the asymmetry of the hydroxyl radical concentration ([OH]) between the NH and SH. The faster the exchange rate constant, the greater the asymmetry, confirming one of the conclusions by Singh (1977). The dissipation constant is less sensitive to an alteration in the exchange constant in the stratosphere than it is to an alteration in the interhemispheric exchange constant. A 50 percent increase in k_5 causes only a 10 percent decrease in the degradation constant.

Mass balance analysis indicates that only 2 percent of total MCF emissions are found in the ocean (Neely and Plonka 1978). Consequently, the degradation in this environmental compartment is not a significant loss mechanism; it is neglected in the present study.

TABLE 3-4. SUMMARY OF STATISTICAL DETERMINATION OF THE DISSIPATING RATE CONSTANTS k_6 AND k_7[a]

Rate constant	Simulated Value (per yr) Simulation I	 II	 III
k_3 & k_4	0.71	0.71	0.86
k_5	0.02	0.03	0.02
k_6 estimated	0.13	0.11	0.072
k_7 estimated	0.17	0.16	0.24

	Calculated Concentrations of MCF[b] in the Northern Troposphere (ppt) I	 II	 III
1972.0	39.8	39.8	39.9
1973.5	51.1	51.1	51.1
1974.5	64.3	64.3	64.3
1974.9	69.3	69.3	69.2
1976.0	80.9	80.9	80.9
1976.2	83.0	83.0	83.0
1976.3	83.8	83.8	83.9
1976.5	86.0	86.0	86.0
1978.0	103.1	103.1	103.2

	Estimated Future Concentrations of MCF (ppt) North	 South
1979	115	80
1980	88	76.6
1981	72.6	68.8
1982	61.1	58.8
1984	43.9	42.4
1986	31.2	30.5
1988	22.7	21.9

[a] Average $k = \dfrac{k_6[N] + k_7[S]}{[N] + [S]} = 0.15/\text{yr}$

Residence time = 6.6 yr

$t_{1/2} = \dfrac{\ln 2}{0.15} = 4.5$ yr

[b] Production terminated in 1978 for Simulation I

Mechanistic Approach

In this technique the major dissipating reaction of MCF in the troposphere is assumed to be via OH attack. Ample evidence indicates that this process regulates the degradation of CFM's (Darnall et al. 1976).

Three items are required to evaluate a tropospheric degradation rate constant for MCF: (1) a value for average [OH] in the troposphere (see Table 3-5); (2) knowledge of the bimolecular rate constant for the attack of OH on MCF; and (3) a value for the average temperature in the troposphere. Of these three items, the assumptions dealing with temperature and [OH] are the least valid. However, if valid numbers could be determined, then unquestionably a tropospheric residence time could be evaluated for MCF by this technique.

TABLE 3-5. AVERAGE TROPOSPHERIC HYDROXYL RADICAL CONCENTRATIONS[a]

Global Average Concentration	Northern Troposphere Concentration	North/South Ratio	Basis	Reference
7.5 (yearly average)			Photochemical models of OH production	Warneck (1975)
	8.0		CO studies	Stevens (personal communication)
	2.5	0.36	Photochemical models of CO and CH_4	Crutzen and Fishman (1977)
	5.0 (average for fall day)		Photochemical model	Crutzen (1974)
7.6			Fourier analysis of seasonal distribution of OH	Derwent and Eggleton (1977)

[a] All concentrations are reported in 10^5 molecules/cm^3.

OH concentrations estimated by a number of investigators are shown in Table 3-5. In this collection, [OH] based on MCF is not included, to avoid biasing the determination of MCF residence time.

The average value for [OH] appears to be in the range of 6×10^5 molecules/cm^3. A degree of controversy surrounds the asymmetry of the concentration between the NH and SH. Values ranging from 1 (Fishman and Crutzen 1978) to 0.25 (Neely and Plonka 1978) have been suggested. Crutzen and Fishman (1977) established a ratio of 0.36 with a higher value in the SH; this value is here used to estimate [OH] in the SH, even though the concentration is also uncertain. The asymmetry is normally explained on the basis of greater carbon monoxide (CO) production in the NH than in the SH and the ability of CO to act as a sink for OH.

Table 3-6 lists various determinations for the rate constant shown in Equation 3.

$$CH_3CCl_3 + OH \xrightarrow{k} CH_2CCl_3 + H_2O \qquad \text{(Eq. 3)}$$

An average value of $\sim 3.1 \times 10^{-12} \exp(-1507/T)$ is used in the following analysis.

The final number required is a time-weighted average of the tropospheric temperature. Temperatures in the troposphere range from 15° C at sea level to -45° C at 10 km (Neely and Plonka 1978). A value of -8° C is the estimated average (Watson et al. 1977; Davis et al. 1976).

TABLE 3-6. BIMOLECULAR RATE CONSTANT FOR HYDROXYL ATTACK ON METHYL CHLOROFORM

Arrhenius Expression[a] (cm^3 $molecule^{-1}$ s^{-1})	Reference
$1.95 \times 10^{-12} \exp(-1331/T)$	Chang and Kaufmann (1977)
$3.72 \times 10^{-12} \exp(-1627/T)$	Watson et al. (1977)
$3.5 \times 10^{-12} \exp(-1562/T)$	Crutzen et al. (1978)

[a] Average value ≈ $3.1 \times 10^{-12} \exp(-1507/T)$.

The photodegradation rate constant for k_6 and k_7 in Figure 3-1, assuming that the dissipating reactions are caused by OH attack, may now be calculated. Values of k_6 and k_7 are 0.20/yr and 0.55/yr, respectively:

$$k_6 = k \times [OH] \times 3.15 \times 10^7 = 0.2/yr \qquad \text{(Eq. 4)}$$

where $k = 1.05 \times 10^{-14}\ cm^3/molecules^{-1}\ s^{-1}$ at -8° C

$3.15 \times 10^7 = s$ in 1 yr

$[OH] = 6.0 \times 10^5$ molecules/cm^3

$$k_7 = k_6/0.36 = 0.55/yr$$

The average tropospheric cleansing rate is a function of the various rate constants. Where dissipating reactions are dominated by k_6 and k_7, as in Figure 3-1, the model is reduced to the set of reactions shown in Equation 5:

$$\begin{tikzcd} A \arrow[r, shift left, "k_3"] \arrow[d] & B \arrow[l, shift left, "k_4"] \arrow[d] \\ k_6 & k_7 \end{tikzcd} \qquad \text{(Eq. 5)}$$

where A and B represent the concentrations of the chemical at any time in the northern and southern troposphere, respectively.

Setting $k_3 = k_4$, the differential Equations 6 and 7 may be readily solved, yielding the solution given by Equation 8.

$$\frac{dA}{dt} = k_3A + k_3B - k_6A \qquad \text{(Eq. 6)}$$

$$\frac{dB}{dt} = k_3A - k_3B - k_7B \qquad \text{(Eq. 7)}$$

$$A = \frac{\{A_0(k_3 + k_6 - \alpha) + k_3B_0\}e^{-\alpha t}}{(\beta-\alpha)} + \frac{\{A_0(k_3 + k_6 - \beta) + k_3B_0\}e^{-\beta t}}{(\alpha-\beta)} \qquad \text{(Eq. 8)}$$

where A_0 and B_0 = initial concentrations

$$\alpha = \frac{D + \sqrt{D^2 - C}}{2}$$

$$\beta = \frac{D - \sqrt{D^2 - C}}{2}$$

$$D = 2k_3 + k_6 + k_7$$

$$C = 4(k_3k_6 + k_3k_7 + k_6k_7)$$

Since $e^{-\alpha t}$ reaches zero much faster than $e^{-\beta t}$, the dissipation is governed by the expression for β. For the situation where k_3 = 0.86/yr, k_6 = 0.2/yr, and k_7 = 0.55/yr, β has a value of 0.36/yr, or an average residence time of 2.78 yr. In the case of the statistical model, the average residence time is 6.6 yr (Table 3-4). Considering the assumptions, the agreement is reasonable and falls within the previously reported range of 1 to 8 yr.

The two main factors to be tested for sensitivity in the mechanistic model are temperature and [OH]. With [OH] constant at 6×10^5 molecules/cm^3, the rate constant is estimated to vary by ~5 percent for every 1 percent change in the absolute temperature. Similarly, if temperature is constant at -8° C, k_6 shows a 1 percent change for every 1 percent change in [OH]. Here again, uncertainty in estimating the average tropospheric residence time for MCF is reflected. The following discussion is based on residence times ranging between 2.78 and 6.6 yr.

TRANSFER OF CHLORINE FROM METHYL CHLOROFORM TO THE STRATOSPHERE

A relatively high concentration of O_3 is located in a narrow band in the stratosphere. This layer is important because the O_3 molecule is a strong absorber of ultraviolet radiation and hence protects the earth's surface from potentially harmful solar radiation.

The main environmental impact of low-molecular-weight halocarbons is the effect of Cl atoms on the O_3; a quantitative estimate of the Cl atoms reaching this altitude is of vital concern and is given by:

$$B = k_5 (A \times 1.4 \times 10^{20} \times \text{molecular weight}) \qquad \text{(Eq. 9)}$$

where k_5 = exchange to the stratosphere

A = global average tropospheric concentration (on a mol/mol basis)

1.4×10^{20} = number of molecules of air in troposphere

For 1978 the global average MCF concentration was reported by Rowland (unpublished) to be 82 ppt. The flux (B) into the stratosphere, assuming 0.02/yr as a value of k_5, ranges from 30.5×10^9 to 24.2×10^9 g of Cl atoms for the year 1977.

The usual yardstick for measuring such a flux is to compare it with the reported analysis for CFM. In the 1977 National Academy of Sciences (NAS) study of CFM, production of FC-11 and FC-12 was assumed constant at the 1973 level. At steady state, this level produces a flux of 500×10^9 g of Cl atoms into the stratosphere. The same scenario of steady-state annual MCF production, at the 1978 rate of 1100×10^6 pounds/yr or 396×10^9 g of Cl atoms, would introduce 20.84×10^9 - 46.6×10^9 g Cl atoms/yr into the stratosphere, with the calculated value depending on the residence time used (2.8 to 6.6 yr). These figures amount to 6 to 12 percent of the annual production. On an arbitrary scale, MCF impact is more than an order of magnitude less than the CFM impact.

The MCF impact would reach the CFM level of effect after ~38 to 55 yr at 6 percent annual growth. If, during this time period, a real problem was perceived, the tropospheric MCF concentration could quickly be reduced because of the relatively short residence time; i.e., the tropospheric concentration could be reduced by 1/2 every 2 to 4.5 yr.

The amount of MCF ultimately reaching the stratospheric O_3 may be considerably less than 6 to 12 percent. In the lower stratosphere (below the major O_3 layer), [OH] is sufficiently great (Crutzen and Fishman 1977) and diffusion sufficiently slow (McConnell and Schiff 1978; Cicerone et al. 1974) that more MCF than previously estimated (solely on tropospheric reactions) may degrade before reaching the O_3 layer. MCF is concluded to be less efficient in destroying O_3 than are the CFM's (McConnell and Schiff 1978). This area needs further investigation.

IMPACT OF CHLORINE ATOMS ON STRATOSPHERIC OZONE

Before discussing the impact of these atoms on O_3, it is useful to review the major reactions associated with formation and destruction of this gas layer.

O_3 is formed through Equations 10 and 11:

$$O_2 + hu \rightarrow 2\ O \qquad \text{(Eq. 10)}$$

$$O + O_2 \overset{M}{\rightarrow} O_3 \qquad \text{(Eq. 11)}$$

Once formed, the layer is maintained at a steady-state level by means of cyclic destruction mechanisms (Table 3-7).

Cycle 4 of Table 3-7 was identified as a possible loss mechanism by Cicerone et al. (1974) and Molina and Rowland (1974b). Theoretically, continued increase in the use of stable halocarbons will cause Cycle 4 to become more dominant; reduced O_3 concentration in the stratosphere will result.

The researcher's information base for the nature or magnitude of the Cl atom impact suffers from a lack of good rate data for known important reactions and from a lack of awareness of all reactions involved. Growing understanding in this field of chemistry will be most useful in establishing a better basis for decision-making.

TABLE 3-7. STRATOSPERIC OZONE DESTRUCTION MECHANISMS

Cycle	Mechanism	Percent Destruction
1	$O_3 + hu \rightarrow O_2 + O$ $O + O_3 \rightarrow 2O_2$	20
2	$O + HO_2 \rightarrow OH + O_2$ $HO + O_3 \rightarrow HO_2 + O_2$	10
3	$O + NO_2 \rightarrow NO + O_2$ $NO + O_3 \rightarrow O_2 + NO_2$	69
4	$O + ClO \rightarrow Cl + O_2$ $Cl + O_3 \rightarrow ClO + O_2$	0.5
5	Loss of O_3 from stratosphere to troposphere	0.5

FURTHER QUESTIONS AND RECOMMENDATIONS

The remainder of this report lists areas where questions are raised and indicates where more work is required. The chlorine cycle (Cycle 4 of Table 3-7) may be interrupted by conversion of Cl into an inactive species. Equations 12 through 14 represent three such reactions:

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad \text{(Eq. 12)}$$

$$ClO + NO_2 \rightarrow ClONO_2 \qquad \text{(Eq. 13)}$$

$$OH + Cl \rightarrow HOCl \qquad \text{(Eq. 14)}$$

Some evidence exists indicating hypochlorous acid (HOCl) is a reservoir for OH and Cl (National Academy of Sciences 1977). If so, additional Cl might conceivably cause an O_3 increase by interfering with Cycle 2 (Table 3-7). However, a report conclusion is: "ClOH, like $ClONO_2$, may be a temporary pseudo-inert reservoir species, although the likelihood of a major impact on the ClO_x cycle appears to be small" (National Academy of Sciences 1977).

More disturbing than the observation that HOCl may act as a sink is that stratospheric chlorine monoxide radical (ClO) measurements are much higher than could be expected if all known Cl-containing compounds were converted to ClO (National Academy of Sciences 1977). Only two explanations seem possible, according to the NAS report — either the measurements are in error, or the possible existence of some unidentified source of Cl in the stratosphere is indicated. This question must be resolved expediently to determine the true impact of man-made halocarbons on stratospheric O_3.

At one time, increased use of nitrogen fertilizer and/or increased numbers of supersonic transports were believed to have a catastrophic effect on the O_3 layer (National Academy of Sciences 1976; Johnston 1975). These assumptions were related to an increased stratospheric NO_x level and increased O_3 depletion due to Cycle 3 (Table 3-7). New studies (Turco et al. 1978) have modified this view, and predictions are for an increase in O_3 below 25 km, due to the higher levels of NO_x and water vapor. The question thus arises as to the possible environmental effects of an increased level of O_3, as opposed to a decreased concentration. In addition, NAS has previously reported that the revised rate constants for some of the reactions related to the odd nitrogen cycle indicate that Cycle 3 is not as important as earlier thought (National Academy of Sciences 1977). Consequent to this assessment has been the speculation that Cycle 4 is more important; the decrease in O_3 depletion from Cycle 3 has been replaced by an increase in O_3 depletion from Cycle 4. One firm conclusion of all the stratospheric chemistry research was reiterated by NAS: "It is now completely clear that all the major chemical catalytic cycles are closely coupled and cannot be studied separately" (National Academy of Sciences 1977).

An interesting study relating to the rates of all the reactions in the stratosphere was recently published (Groves et al. 1978). The authors suggest that increased stratospheric carbon dioxide (CO_2) levels will cause worldwide cooling. Since Equations 10 and 11 proceed faster at lower temperatures, but the various destructive cycles proceed more slowly, the expected net result is an increase in O_3. The CFM's were compared with and without the added effects of CO_2. The decrease in O_3 column density attributed to CFM by the year 2030 was 4 percent, assuming a continued steady release at 1973 rates, with a steady-state reduction of 6 to 7 percent a few decades later. The corresponding figure in the year 2030, incorporating the temperature effect of CO_2, amounted to a 5 percent increase in the O_3 layer. Without CFM's, the increase might be even higher.

A recent laboratory-simulation study of the upper atmosphere (Benson 1978) showed a lack of sensitivity to CFM concentrations varying over 4 orders of magnitude. This laboratory-simulation study parallels recent studies from the Goddard Space Flight Center (Air/Water Pollution Report 1978). Using satellites to monitor the upper atmosphere, the measurements indicated that deterioration of the stratospheric O_3 is 1/2 the amount deduced from ground measurements.

While undoubtedly some of the Cl-containing molecules reach the stratosphere, their exact impact is uncertain. Since the impact is not known with any degree of confidence and in view of the safety valve on MCF in terms of a relatively fast half-life, the conclusion of Dow Chemical Company is that MCF must be very low on the priority list of potential environmental hazards.

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DISCUSSION

Dr. Heicklen: Your calculations yield slightly more optimistic estimates. Instead of using the product of the average OH times the average temperature times the average concentration, you used the average of the products. Of course, where the OH is highest is where the temperature is highest; the rate coefficient will go up the most, probably another 10 or 12 percent. It is appropriate to use the average of the products, not the product of the averages.

Dr. Neely: Good. Thank you.

Voice from Audience: Do you feel very confident about estimating a 6 percent per year increase in demand for MCF? How do you folks arrive at these figures, and how well will they hold for the future? We are interested in the validity of other sorts of estimates, also.

Dr. Neely: Since I'm not in the department of the marketing groups, Dr. Farber, would you respond?

Dr. Farber: Only incomplete data are available for formulating estimates; however, the estimates are based on expected growth in recognized use areas, which is dependent on the GNP in this country and on worldwide product usage; on expected growth in use of available alternates; and on the economics for the user. These are gut decisions that we make, and sometimes not well, if the discrepancy between the capacity and the market for perchloroethylene is considered. But I think the 6 percent is based on a combination of expected growth of the general GNP here and worldwide, in the European area primarily, so that is a global number in the economics of the products used. Does that help?

Voice from Audience: Do you associate an uncertainty with that?

Dr. Farber: Plus or minus 100 percent from that. In other words, I don't expect to see attrition of the product, barring some unforeseen unfortunate experience; and I don't expect to see 12 percent average over the next 5 yr. 5 yr is the best time frame to use, really. Historically, MCF emissions have displayed peaks and valleys, and in Dr. Neely's first slide [Table 3-1], quite a dramatic growth is seen in the last 2 or 3 yr. The actual numbers turn out to be in a range between -1 percent and +12 percent; the average of that, over the last 5 yr, is ~5 percent, I think. We project about the same rate fluctuation: we expect to see years where pressures, of whatever nature, cause increases in the 10-percent range; we expect to see years where things are bad and we see a net loss in the product's use.

Dr. Singh: The emission inventory statements you have provided — and I guess that is exactly what Dr. Neely has used — show exponential growth rate over the last 10 or 12 yr of ~17 percent average for MCF emissions as well as for global production; that would be the average if you put it in a log plot.

Dr. Neely: I think that is right. I think if you put it into a log model, an exponential model, for the last 16 yr, it comes out to 16.5 percent. I have these percentages on a table [Table 3-1] in the manuscript. Beginning with 1962, a 9.6 percent decrease is seen, then percent increases of 11, 28, 49, 20, 11, 2.19, 4.28, 7.9, 38, 6.67, 0.5, 47.6, 14.05, 6.87, 12.2. Average change over the last few years is ~16, but the percent change fluctuates. Our best estimate for the fluctuation in the next few years is ~6 percent.

Voice from Audience: For the uninitiated of us, are you giving us figures for capacity or production? Do you have excess capacity or not currently?

Dr. Neely: These figures are a best estimate of emission. I think we have excess capacity. Right.

Dr. Rowland: I have two questions. First: What accuracy do you attribute to the estimates of the world production of MCF that are used in these calculations?

Dr. Fari . I would comment for the Western World and the Free World in the East outside the Communist bloc. I doubt that much production occurs in China, but I know the products are used in Russia. Disregarding whatever input exists from the Communist bloc, we're accurate within 10 percent for sure.

Dr. Rowland: The other question is: For what fraction of that production is Dow Chemical responsible?

Dr. Farber: I don't have an exact number, but ~50 percent on a global basis. If you really need to know that for your modeling, I will be glad to get it for you.

Dr. Rasmussen: I have one slide: these are our best calculations at the moment for the past 3 yr, integrating the concentrations in both hemispheres. Surprising to us is that between 1977 and 1978 the mass burden of MCF in the NH increased only 7 percent. This rate does not fit with Dr. Rowland's increase per month figure.

The internal consistency in our calibration standards from 1976, 1977, 1978, and through 1979, shows ±~2 or ~3 ppt variance in the primary standards. Previously, with less extensive data in both hemispheres and less coverage in time, we had calculated a much larger growth rate. The value for 1978 represents something on the order of up to 200 measurements. The MCF data from the Manufacturing Chemists Association program in the SH indicate a very ~low order of change in the SH.

HALOGENATED TRACE CONSTITUENTS IN THE GLOBAL ATMOSPHERE

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DISTRIBUTIONS, SOURCES, AND SINKS OF HALOGENATED TRACE CONSTITUENTS

Distributions

Most estimates of the budgets and residence times of halocarbons have been based on point measurements, and the hemispheres have been assumed to be well mixed. Recently, Singh et al. (1979) presented extensive global measurements of several halogenated and nonhalogenated species and characterized their growth rates over a period of 3 yr. This global distribution covered an area between 64° N and 90° S latitudes at widely varying longitudes.

Figure 4-1 shows the global distribution of many halocarbons for late 1977. For all stable halogenated species (fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2, FC-12), fluorocarbon-11 (trichlorofluoromethane, CCl_3F, FC-11), fluorocarbon-113 (CCl_2FCClF_2, FC-113), fluorocarbon-114 ($CClF_2CClF_2$, FC-114), sulfur hexafluoride (SF_6), and carbon tetrachloride (CCl_4)), the average concentration in the Northern Hemisphere (NH) and Southern Hemisphere (SH) differs only marginally (10 to 15 percent). Using the emissions data for FC-12 and FC-11 (Manufacturing Chemists Association 1978) an interhemispheric exchange rate (τ_e) of 1.2 yr can be calculated. Figure 4-1 also shows the global distribution of methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3,

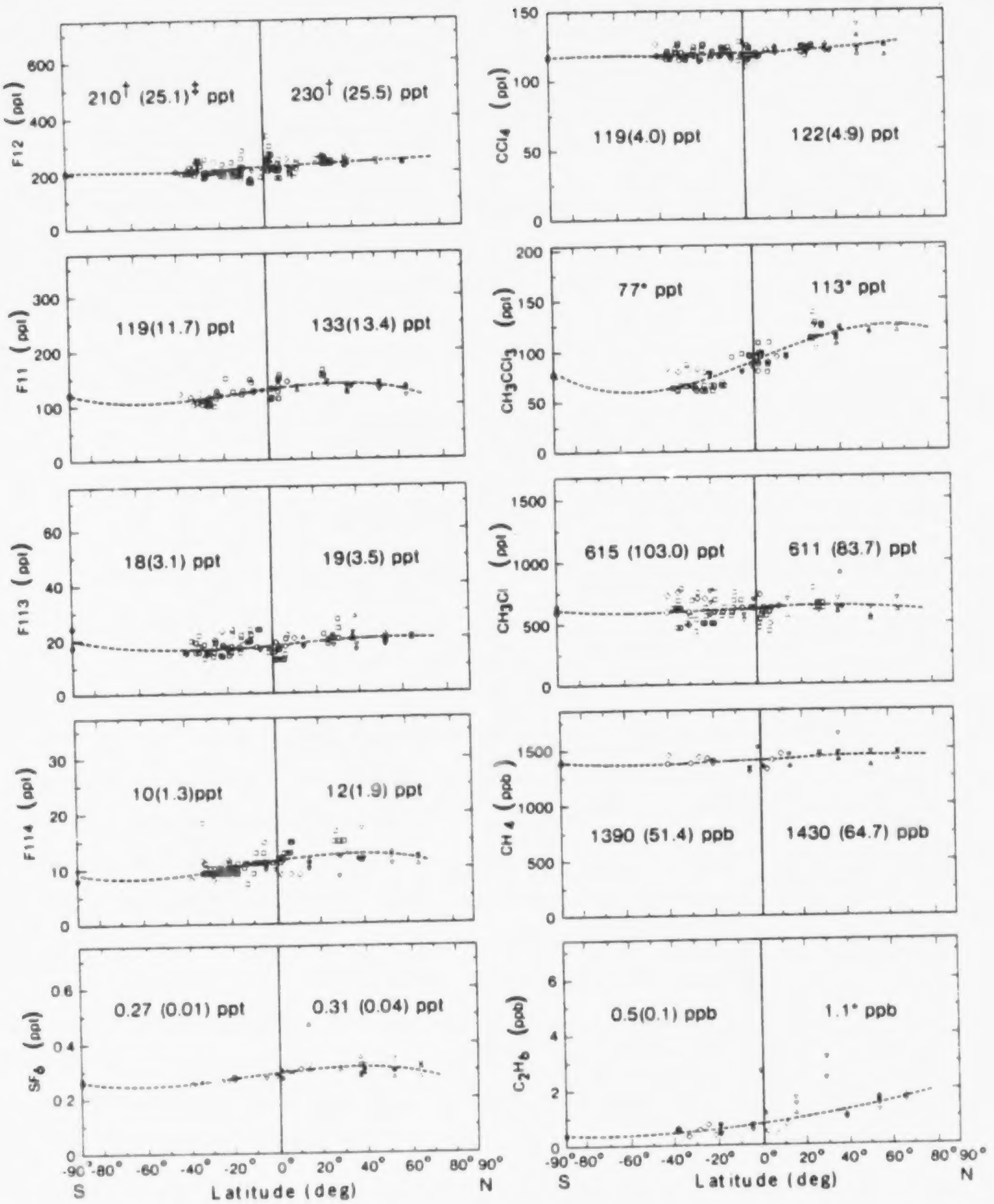

Figure 4-1. Global distributions of atmospheric constituents. Key: ppt = 10^{-12} (v/v); ppb = 10^{-9} (v/v); (†) is the average concentration in the hemisphere; (‡) is the standard deviation; (*) indicates that for species where a significant gradient within each hemisphere is observed the weighted average concentration is defined to represent the total burden of the species in that hemisphere; ∇, trip 1, stainless steel vessels; Δ, trip 1, glass vessels; ◊, trip 2, stainless steel vessels; and □, trip 2, in-situ air sampling and analysis. The dashed line is a third-order polynomial fitted to the data. In most cases, individual hemispheres can be treated as well mixed. In the case of CH_3CCl_3 and C_2H_6, where this is not true, the global profile is well represented by the polynomial $89.71 + 0.818\,L + 7.584 \times 10^{-4}L^2 - 7.894 \times 10^{-5}L^3$ for CH_3CCl_3 and $0.769 + 9.926 \times 10^{-3}L + 6.526 \times 10^{-5}L^2 + 5.561 \times 10^{-8}L^3$ for C_2H_6, where L is the latitude (in degrees) and varies from -90° to +64° (NH = 0° to +90°; SH = 0° to -90°).

MCF) and a third-order polynomial fitted to it. This compound shows a latitudinal distribution quite different from that of the fluorocarbons. In latitudes above 30° N, the MCF is well mixed in the NH with an average concentration of ~123 ppt. A fairly sharp decline seems to occur between 20° N and 20° S, and the concentration of MCF then levels off to ~75 ppt. The decline cannot be attributed to normal mixing processes, since fluorocarbons do not show this rapid decline. A more plausible explanation of this phenomenon is that the hydroxyl radical (OH) is more abundant around the equator because of the intense sunlight and the high concentration of water vapor in this region. The weighted average of MCF concentrations, ~113 ppt in the NH and ~77 ppt in the SH, best describes the burden of MCF in each hemisphere.

Methyl chloride (CH_3Cl) had been measured in the NH by numerous researchers, but no SH data had been available. Figure 4-1 shows an essentially uniform global distribution, with an average global concentration of 615 ppt. The relatively short lifetime of CH_3Cl (2 to 3 yr) and its uniform global distribution support the idea of a large natural source. The primary man-made emissions of CH_3Cl had been thought to be negligible. To the contrary, however, CH_3Cl concentrations of nearly 2200 ppt were found in Lisbon. The Los Angeles vicinity (Riverside) showed an average CH_3Cl concentration of 1500 ± 700 ppt (maximum 3800 ppt), ~2.5 times the background measured concentrations (Singh et al. 1978b). Thus, a significant urban source of CH_3Cl seems to exist. The possibility that automobile exhaust or other combustion processes may be such a source should be investigated.

Growth Rates

Figure 4-2 shows the growth rates of FC-12, FC-11, CCl_4, and MCF, four of the most important man-made halocarbons, in the north temperate regions. Despite a recent decline in the use of fluorocarbons, the atmospheric burdens of FC-12 and FC-11 clearly increased at rates of ~19 ppt/yr and ~13 ppt/yr, respectively. CCl_4 increased at a rate of ~2 ppt/yr, while MCF increased at ~16 ppt/yr. The atmospheric growth of these halocarbons is consistent with the available emissions data (Singh et al. 1976; 1979).

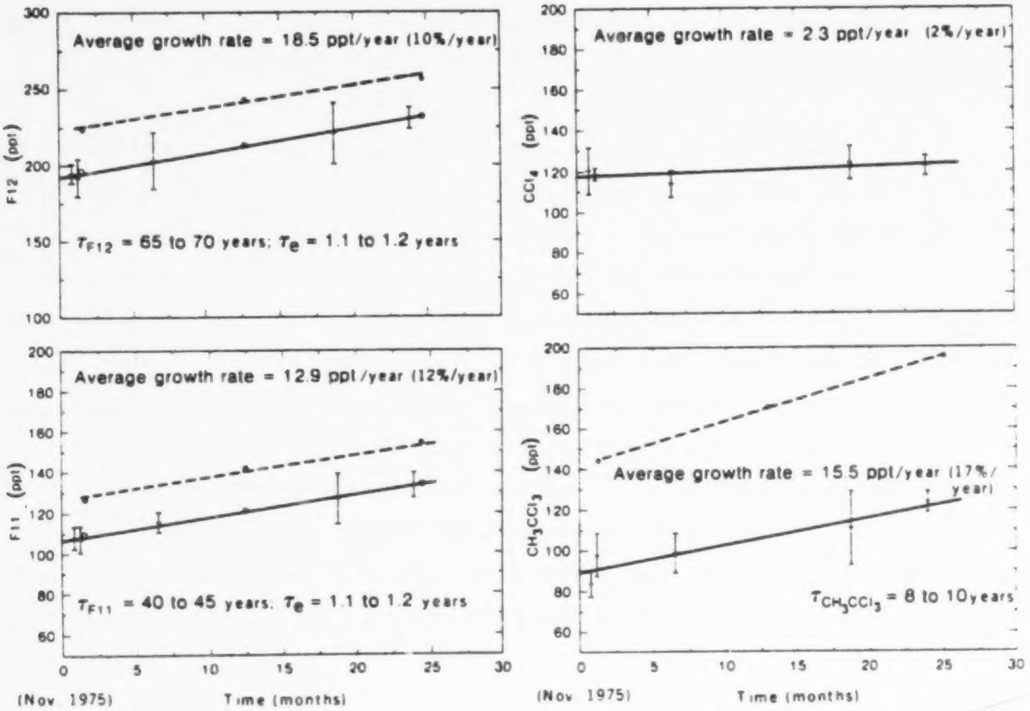

Figure 4-2. Atmospheric growth of FC-12, FC-11, CCl_4, and CH_3CCl_3. The solid line shows the average growth based on data measured between 35°N and 65°N, a region of essentially uniform concentration. The dashed line indicates the concentration at 35°N to 65°N that would result if the cumulative emissions were distributed globally according to the distribution shown in Figure 4-1. The difference between the dashed and the solid lines is indicative of the amount lost to atmospheric sinks. The circles indicate the predicted concentration in the NH from emissions data and the range of indicated residence times. The interhemispheric exchange rate (τ_e) fits the average north-south distribution of FC-12 and FC-11 corresponding to the period and measurements shown in Figure 4-1.

TABLE 4-1. TROPOSPHERIC CONCENTRATIONS OF IMPORTANT ATMOSPHERIC TRACE CONSTITUENTS[a]

Compound Group	Chemicals	Source[b]	Data Quality[c]	Volumetric Mixing Ratio[d]		Average Atmospheric Growth Rate Between 1975-1977
				NH	SH	
Nitrogen compounds	N_2O	N	2	310 ppb	310 ppb	0-1 ppb/yr
Fluorinated (nonchlorinated) species	CF_4 (FC-14)	A (?)	3	65 ppt	65 ppt	
	SF_6	A	2	0.3 ppt	0.3 ppt	
Chlorofluoro-carbons	CCl_2F_2 (FC-12)	A	2	250 ppt	225 ppt	19 ppt/yr
	CCl_3F (FC-11)	A	2	150 ppt	135 ppt	13 ppt/yr
	CCl_2FCClF_2 (FC-113)	A	2	20 ppt	18 ppt	
	$CClF_2CClF_2$ (FC-114)	A	2	12 ppt	10 ppt	
	$CHCl_2F$ (FC-21)	A	3	5 ppt	4 ppt	
Chlorocarbons	CH_3Cl	N	2	611 ppt	615 ppt	
	CCl_4	A	2	122 ppt	119 ppt	2 ppt/yr
	CH_3CCl_3	A	2	113 ppt	77 ppt	16 ppt/yr
	CH_2Cl_2	A	3	44 ppt	20 ppt	
	C_2Cl_4	A	3	40 ppt	12 ppt	
	C_2HCl_3	A	3	16 ppt	<3 ppt	
	$CHCl_3$	A	3	14 ppt	≤3 ppt	
	C_2Cl_6	A	3	≤5 ppt	-	
Brominated species	CH_3Br	N,A	3	5-20 ppt	-	
	CH_2Br CH_2Br	A	3	≤5 ppt	-	
Iodated species	CH_3I	N	3	<2 ppt	<2 ppt	
Hydrocarbons CO, CO_2, and H_2	CH_4	N,A	2	1600 ppb	1500 ppb	
	C_2H_6	N,A	3	1 ppb	0.5 ppb	
	C_2H_2	A	3	<0.2 ppb	<0.2 ppb	
	CO	N,A	2	100-250 ppb	60 ppb	
	CO_2	N,A	1	336 ppm	334 ppm	
	H_2	N,A	2	580 ppb	550 ppb	

[a] As of early 1978.

[b] N — natural, A — anthropogenic.

[c] 1 — excellent data base with uncertainties ≤5 percent
2 — fair data base with uncertainties <15 percent
3 — fragmentary information.

[d] ppm = 10^{-6} v/v; ppb = 10^{-9} v/v; ppt = 10^{-12} v/v.

Budgets

Table 4-1 shows average concentrations of trace constituents of interest in the two hemispheres. The data are from several sources: most halocarbon data are taken from Singh et al. (1979); the fluorocarbon-14 (carbon tetrafluoride, CF_4, CF-14) data are taken from Rasmussen et al. (1979). The halocarbon sources are shown and the data quality is categorized. Also shown are the average growth rates of important halocarbons.

Table 4-2 provides total tropospheric budgets of organic Cl, Br, I, and F, and indicates source contributions. The global average tropospheric Cl concentration (organic) for late 1977 is 2.7 ppb, implying that the maximum Cl measured near 40 km should be <2.5 ppb. The possibility that unknown sources of tropospheric Cl exist cannot be completely dismissed, but measurements of total organic Cl (Berg and Winchester 1976) do not support the existence of large unknown Cl sources. Of the total 2.7 ppb Cl, ~77 percent is man-made and the remaining ~23 percent appears to be of natural origin.

TABLE 4-2. TROPOSPHERIC CHLORINE, BROMINE, IODINE, AND FLUORINE ORGANIC BUDGETS

Species	Budgets			Source Contributions (%)	
	NH	SH	Globe	N[a]	A[b]
Cl	2.9 ppb	2.4 ppb	2.7 ppb	23	77
Br	10-30 ppt	-	-	50-90	10-50
I	<2 ppt	<2 ppt	<2 ppt	100	0
F	1.0 ppb	0.9 ppb	1.0 ppb	0	100

[a] N — natural.
[b] A — anthropogenic.

The organic Br and I budgets are much more uncertain. Measurements by Singh et al. (1979) suggest only two brominated species, methyl bromide (CH_3Br) and ethylene dibromide (CH_2BrCH_2Br). Even for these two species the data base is highly scarce (see Table 4-1). A preliminary interpretation suggests an organic Br content of 10 to 30 ppt, of which 50 to 90 percent may be of natural origin (Table 4-2).

No significant sources of organic I appear to exist. The only species identified currently is methyl iodide (CH_3I), which is present at a concentration of ~2 to ~5 ppt in the marine boundary layer. The tropospheric mean concentration of CH_3I is expected to be much less than 2 ppt. The atmospheric residence time of CH_3I is ~5 days.

The Cl, Br, and I budgets are contrasted with the budget for F, which shows ~1 ppb of F almost entirely attributable to man-made sources. Very possibly other sources of organic Br and I are yet to be identified. Special emphasis should be devoted to identification of new species and better characterization of those already measured.

Oceanic Sink

Halocarbons were also measured in Pacific seawater, primarily to determine the ability of the ocean to act as a source or a sink for them. The average surface concentrations of individual species are given in Table 4-3. The average measured surface-water concentrations (expressed in ng/liter) were: FC-12, 0.28; FC-11, 0.13; CCl_4, 0.40; CH_3Cl, 26.28; and trichloromethane (chloroform, $CHCl_3$), <0.05. With the surface-water concentrations of halocarbons known, a simple film-diffusion model of the flux of halocarbons into or out of the ocean can be determined (Junge 1976; Singh et al. 1978a):

$$F = \frac{D}{Z}\left(C^{w} - C^{w}_{eq}\right) \qquad \text{(Eq. 1)}$$

where F = the flux from ocean to air
D = diffusion coefficient
Z = film thickness
C^{w} = concentration of the species in water
C^{w}_{eq} = concentration in equilibrium with the burden in air

TABLE 4-3. OCEANIC SINKS

Compounds	Average Surface Concentration (ng/liter)	Flux into the Ocean	T_o (yr)
FC-12	0.28 (>0.05[a]) (Min 0.07)	very small	very large
FC-11	0.13 (>0.06[a]) (Min 0.07)	very small	very large
CCl_4	0.4	$+3.2 \times 10^{10}$ g/yr	100
CH_3Cl	26.8	-3×10^{12} g/yr	~2

[a]Saturation concentration.

Solubility data for FC-12 and FC-11 (Junge 1976) suggest that, if the surface water is in equilibrium with the atmospheric burden, the concentrations of FC-12 and FC-11 in water should be ~0.05 and ~0.06 ng/liter, respectively. These concentrations are lower than the measured average concentrations of 0.28 and 0.13 ng/liter, indicating that ocean water is supersaturated with FC-12 and FC-11. Therefore, either the solubility data are inaccurate or the water samples were inadvertently contaminated. Another possibility is that the ocean surface waters have been contaminated by man-made activities on a global scale. The lowest concentration of FC-12 and FC-11 measured, 0.07 ng/liter, is about what one would expect if the surface water were saturated with FC-12 and FC-11. If the surface water were saturated, the ocean would be a relatively ineffective sink for FC-12 and FC-11 but could act as a reservoir containing <0.5 percent of the atmospheric burden of FC-12 and FC-11 in a steady-state situation.

The average surface water concentration for CCl_4 was 0.40 ng/liter. The flux of CCl_4 into the ocean can be calculated from Equation 1, with $D = 10^{-5}$ $cm^2\ s^{-1}$, $Z = 90\ \mu m$, and $S_{CCl_4} = 0.85$. The solubility, S, in seawater is defined as the ratio of the species concentration at the air-sea interface (C_{eq}^{w}) to the atmospheric concentration at standard temperature and pressure. A high Z is used because CCl_4 is rapidly absorbed in fatty tissues and may be biologically active. For such species the upper limit of the stagnant film thickness calculated from random data (63 ± 30 μm) is more appropriate. Using Equation 1, a CCl_4 flux into the ocean of 2.8×10^{-16} g cm^{-2} s^{-1} can be calculated. If this flux is assumed typical of all oceans, an exchange rate of 3.2×10^{10} g/yr is obtained. The atmospheric burden of CCl_4 from the measurements is calculated as 3.2×10^{12} g. Thus the ocean is a sink for CCl_4 that can provide a turnover rate of 100 yr ($\tau_{CCl_4} = 3.2 \times 10^{12}/3.2 \times 10^{10}$). These measurements thus indicate that the oceanic sink for CCl_4 is about half as effective as the stratospheric sink.

The surface concentration of CH_3Cl in the Pacific is quite variable (Table 4-3), with values somewhat higher near the equator. The average surface concentration was 26.8 ng/liter. Using an S_{CH_3Cl} of 2.65 (Dilling 1977) and other parameters as defined earlier, a CH_3Cl flux from the ocean to the atmosphere of 2.6×10^{-14} g cm^{-2} s^{-1} is estimated. Extending this flux to the world ocean body gives an exchange rate of 3.0×10^{12} g/yr. From these measurements, the atmospheric burden of CH_3Cl can be estimated as 5.5×10^{12} g. Thus, on the basis of limited data, the ocean appears to be a significant source of CH_3Cl, which can provide an atmospheric turnover rate of ~2 yr. This rate is in reasonable agreement with the estimated CH_3Cl residence time of ~2 to ~3 yr, due to OH attack (OH = 3×10^5 to 5×10^5 molecules/cm^3.

Residence Times

A comparison of emissions data for FC-12 and FC-11, with the help of a two-box model, suggests an average FC-12 residence time of 65 to 70 yr and an average FC-11 residence time of 40 to 45 yr (Singh et al. 1979). Figure 4-2 shows the good agreement between measurements and calculated values. Because of an important oceanic sink, the CCl_4 residence time can be estimated at between 25 and 40 yr. Several estimates of the MCF residence time have been made; these are summarized in Table 4-4. The best estimates of MCF residence time seem to lie between 6 and 12 yr, excluding the outlier point from Neely and Plonka (1978). This range should be compared with the MCF residence time of 1.4 yr reported by the National Academy of Sciences (NAS) (1976). A 6- to 12-yr residence time allows 12 to 25 percent of the MCF released at ground level to enter the stratosphere. This long tropospheric residence time, when coupled with the rapidly increasing emissions, suggests that MCF may be a potential depleter of stratospheric ozone (O_3) in the decades ahead. Worldwide release of MCF to the atmosphere currently approaches 7×10^{11} g/yr and is increasing at a rate of 10 to 15 percent per year. Continued uncontrolled release of MCF to the atmosphere should be a matter of future concern.

TABLE 4-4. GLOBAL AVERAGE RESIDENCE TIME (T_a) OF METHYL CHLOROFORM

Estimated from Field Data	T_a (yr)	Model Estimates	T_a (yr)
Singh (1977a)	7 ± 1	all estimates prior to 1977	1-3
Lovelock (1977)	5-10		
Singh (1977b)	8-11	National Academy of Sciences (1976)	1.4
McConnell and Schiff (1978)	8		
Chang and Penner (1978)	12	Crutzen and Fishman (1977)	10
Krasnec (unpublished, 1979)	9-12 (est.)[a]		
Rowland (unpublished, 1979)	~6 (est.)[a]		
Neely and Plonka (1978)	3[b]		

[a] Estimated by Singh.
[b] Same data as used by Lovelock (1977).

MCF Budget and the Hydroxyl Radical

Inert species such as fluorocarbons and SF_6 are tracers that identify and quantify the global circulation, whereas the distribution of the more reactive halocarbons such as MCF offers a unique means for quantifying the role of OH, a central atmospheric species that cleanses the atmosphere of impurities (Singh, 1977a; 1977b).

Two points are important here: (1) a residence time of 6 to 12 yr for MCF implies a seasonally averaged tropospheric OH abundance of 3 to 6 x 10^5 molecules/cm^3, which is significantly lower than the values estimated from models; and (2) from an analysis of MCF data, the OH distribution in the two hemispheres appears to be asymmetric.

When used in a two-box model together with available emissions data (Singh 1977b), the hemispheric distribution indicates a higher average OH concentration in the SH than in the NH ($(OH)_{SH}/(OH)_{NH} \geq 1.5$). This asymmetric OH distribution can be attributed to carbon monoxide (CO), which is an important atmospheric sink for OH and is three times more abundant in the NH than in the SH. Should the excess CO in the NH be from man-made sources (as is currently believed), additional future depletion of OH in the NH can be expected. The depletion of OH would reduce the scavenging ability of the atmosphere, allowing increasing amounts of pollutants to enter the stratosphere. In addition, the tropospheric reservoir of many natural and man-made species would increase. Two-dimensional global models are required to simulate more precisely the global distribution of MCF and OH.

CURRENT STATUS OF HALOGENATED TRACE CONSTITUENTS

Highlights in the present understanding of halocarbons and their atmospheric effects are given below:

(1) Apparently no significant tropospheric sinks exist for fully halogenated fluorocarbons. The atmospheric burden of these species is increasing at a rate proportional to the emissions burden.

(2) Global distributions of FC-11 and FC-12 suggest a 1.2-yr interhemispheric exchange rate.

(3) Less doubt exists now than ever before that CCl_4 is essentially man-made, but all anthropogenic sources have not been characterized.

(4) The oceans may provide a sink for CCl_4 that is about half as effective as the stratospheric sink.

(5) The maximum Cl atom in the stratosphere is <3 ppb, of which ~75 percent appears to come from man-made sources.

(6) MCF appears to have an atmospheric residence time of 6-12 yr and may be a potential depletor of stratospheric O_3. About 12 to 25 percent of all MCF released to ground level is expected to enter the stratosphere.

(7) Residence time information on MCF can be used to suggest seasonally-averaged OH concentrations of 3 to 6 x 10^5 molecules/cm^3. Thus, removal of all species by reaction with OH may be significantly slower than predicted by models.

(8) The oceans appear to be a dominant source of CH_3Cl. Other sources of CH_3Cl, man-made as well as natural, also exist. The oceanic data show great variability in CH_3Cl distribution. The oceans remain poorly characterized as sources or sinks of halocarbons.

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DISCUSSION

Dr. Rasmussen: One difficulty in obtaining these gradients and interhemispheric ratios, I feel, involves the number of data points and the number of times or the different times during the year that samples were taken or measurements made. There's also the problem of intercalibration. You've heard of

Joe Krasnec's MCF ratio that showed a difference crossing the intertropical convergence zone (ITCZ). And the ratio from data points collected in the NH and the SH on just that one flight across the Pacific was on the order of ~1.28.

Dr. Singh: He is not here, so I will speak on his behalf. His ratio is 1.21, and it's not all that different. I recently talked to him, and this is his final number to be published.

Dr. Rasmussen: His ratio is changed since we last compared data and observed a very small difference. We will both be publishing our results presented at the AGU meeting in December. And sometimes discrepancies are seen on the same flight, and these must be resolved. Another concern is that, to characterize a hemisphere, we must consider the total number of data points necessary. The SH can be characterized reasonably well with a few data points, because homogeneity is good beyond 30° S. In the NH, characterization is difficult from 20° to 60° N, because we found again and again, as did other investigators, considerable variability in MCF. So reconciling differences between laboratories or data presentations, even at this meeting, will be exceedingly difficult until the individual trip reports and data sets are examined. Only then will inspection reveal which data points will fit the modeling objectives.

Dr. Singh: Based on available information, it is not possible to determine the quantity of data required. At this point, it is the quality that is most critical. Typically, the more reactive a given species, the greater need for extensive temporal and spatial data coverage. For MCF, if the residence time is indeed of the order of one decade, the amount of data needed to characterize its atmospheric budget and distribution should not be too terribly large. It is pertinent to add here that our observations are based on our interpretation of the best available atmospheric and emission data. There is little doubt in my mind that the hypothesis proposed here will be better understood and quantified as additional high quality data become available.

Question from Audience: You said, essentially, your global distribution was calculated and integrated without weighting because of insufficient data?

Dr. Singh: No, the atmospheric mass within 10° latitudinal belts was considered. The weighted average concentrations are not merely the averages of measured concentrations. Where data did not exist, they were interpolated.

Dr. Rowland: In the laboratory, a contamination-free measurement was found difficult to achieve for certain compounds, and MCF is one of them. So we tried to measure MCF alone and specifically, resulting in several data points. If no other measurements present problems, one arrives at the same number. In fact, deriving a different number would give reason to doubt the numbers collected, 8 or 10 molecules at a time. FC-21, for instance, raises considerable suspicion, because a Teflon contamination appears to exist. So that's the reason we are attempting to measure MCF differently.

Dr. Singh: Right now we must attribute the 20 ppt difference between our north temperate zone MCF concentrations and those of Dr. Rowland to absolute calibration differences. The important observation is that even Dr. Rowland's data, which are some 20 percent lower than ours, point to a ~6-yr MCF residence time. This is a factor of 4 or more higher than the 1.4-yr residence time recommended by NAS. The current consensus on MCF residence time would be 6 to 12 yr, allowing 12 to 25 percent of all MCF released at ground level to enter the stratosphere.

Dr. Crutzen: I can give you data I obtained yesterday: In the SH marine air, 89 ppt was the average number; in the NH marine air, 96 ppt; and in the NH continental air, 121 ppt. These are probably arithmetic averages of all the numbers, but I don't have the refinement which Dr. Rasmussen just indicated.

STRATOSPHERIC IMPACT RESEARCH AND ASSESSMENT

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INTRODUCTION

The Clean Air Act Amendments of 1977, which are a part of Public Law 95-95, require the U.S. Environmental Protection Agency (EPA) to conduct research on substances, practices, and activities that affect the stratosphere, especially the ozone (O_3) layer. This research includes physical, chemical, atmospheric, and biomedical studies to ascertain the causes and effects of stratospheric change. It also includes methods to recover and recycle, prevent the escape of, and find substitutes for materials that bring about O_3 depletion. Additional research in specific areas is assigned to other Federal agencies, but EPA is required to contract with the National Academy of Sciences (NAS) to study and report on the state of knowledge of O_3 depletion, including health, biological, and socioeconomic effects.

EPA must also study and report on methods to control emissions. In light of requirements to establish a coordinating committee, EPA has created the Interagency Committee on Stratospheric Ozone Protection (ICSOP). EPA has also contracted with NAS for support of two committees. One committee, the Committee on Impacts of Stratospheric Change (CISC), will report on the state of knowledge regarding O_3 depletion. The other, the Committee on Alternatives for the Reduction of Chlorofluoromethanes (CARCE), will report on alternatives for control of emissions and the socioeconomic impacts of control/noncontrol. EPA expects a preliminary report from CISC in the summer of 1979 and a report from CARCE in September. A comprehensive report, anticipated for the end of 1979, will be assimilated into the required biyearly EPA report to Congress due in 1980.

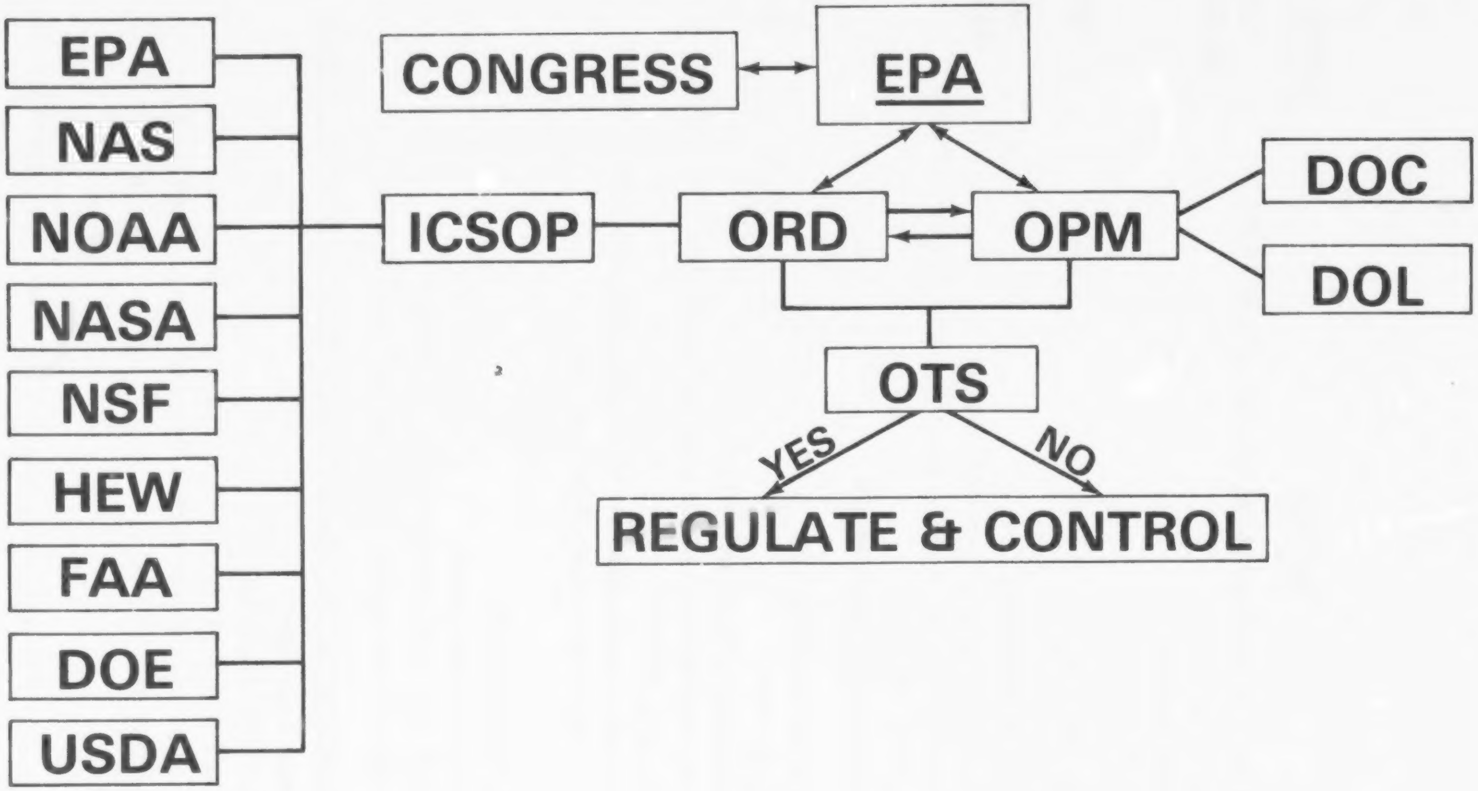
Nine governmental agencies, including EPA, transmit reports of their research to ICSOP. The Committee digests this information and prepares a report to EPA's Office of Research and Development (ORD). The Departments of Commerce and Labor report either to ORD or to the EPA Office of Program Management (OPM). Regardless, the information is exchanged between the two offices and then forwarded to the Office of Toxic Substances (OTS), where a decision of whether or not to regulate is made. All of this exchange takes place in complete coordination with the EPA Administrator's office and is reported to Congress as indicated above (see Figure 5-1).

EPA RESEARCH

Figure 5-2 outlines EPA's major research needs and uncertainties. The first requirement is to know the magnitude and rate of O_3 depletion, which involves study of models and monitoring trends. This work is performed primarily by the National Aeronautics and Space Administration (NASA), the Federal Aviation Administration (FAA), the National Oceanic and Atmospheric Administration (NOAA), and the Department of Energy (DOE) through the Lawrence Livermore Laboratory. The program supports efforts to model climatic effects only in a token manner; EPA is primarily concerned with biological and human effects. But EPA partially supports other areas, as will be discussed later.

EPA's next concern is the change in ultraviolet (UV) radiation associated with the change in O_3 concentration. EPA supports this work primarily through NOAA. In the next area, climatic effects, EPA has recently taken an interest in studying the effects of increased UV radiation on smog, and is considering a small grant to the University of Florida to research this problem.

EPA's interest in biological effects includes crop yields, photosynthesis, growth inhibition and pathological effects on plants, and effects on animals and marine organisms. UV radiation is generally assumed to be unable to


EPA
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NOAA
NASA
NSF
HEW
FAA
DOE
USDA
CONGRESS
EPA
ICSOP
ORD
OPM
DOC
DOL
OTS
YES
NO
REGULATE & CONTROL

Figure 5-1. Information and decision chart.

NEED	**WHO SUPPLIES**
1. HOW MUCH OZONE DEPLETION, HOW FAST ? ● MODELS ● MONITORING ● TRENDS	NASA, FAA, NOAA, DOE (LLL)
2. ΔUVB VS. ΔO_3	NOAA, EPA
3. CLIMATIC EFFECTS ● GLOBAL SURFACE TEMPERATURE ● REGIONAL SURFACE TEMPERATURE AND PRECIPITATION ● STORM TRACKS ● INCREASED URBAN SMOG	NOAA, DOE, NSF, EPA, FAA
4. BIOLOGICAL EFFECTS ● CROP YIELD ● PHOTOSYNTHESIS INHIBITION ● PHOTOMORPHOGENETIC AND PATHOLOGICAL EFFECTS ● ANIMAL EFFECTS ● MARINE ORGANISMS (PHYTO- AND ZOOPLANKTON, LARVAE OF CRUSTACEA AND FISH)	USDA, NSF, NOAA, EPA
5. HEALTH EFFECTS ● UVB AND ERYTHEMA ● UVB AND NON-MELANOMA SKIN CANCER ● UVB AND MELANOMA (MALIGNANT) SKIN CANCER	NCI
6. INTEGRATED ASSESSMENT AND CONTROL STRATEGIES ● RISK ANALYSIS ● BENEFIT ANALYSIS ● CONTROL ANALYSIS (PRODUCTION BAN, EMISSION BAN, RECOVERY, SUBSTITUTES, INTERNATIONAL CONTROLS, COST INCENTIVES)	EPA, DOC DOL

Figure 5-2. Major data needs and uncertainties.

penetrate water to any significant extent; therefore, no marine effects should occur from radiation. But they do occur, revealing that UV penetrates water more than previously believed. Consequently, many aquatic organisms that spend a significant amount of time in the uppermost layer of water bodies are affected.

Turning to human health effects, the degree of a sunburn is directly correlated with increased exposure to UV radiation — a relationship that is very well established. But the correlations involved with incidence of plain skin cancer (i.e., nonmelanoma skin cancer) or melanoma skin cancer are less certain, as are factors that are distinct between the two cancers. EPA is striving to clarify these issues, because melanoma skin cancer is rapidly increasing in the United States.

With reference to Item 6 of Figure 5-2, EPA is the only agency that is specifically required to make a complete, integrated assessment of all aspects of O_3 depletion and to report this assessment to Congress. This task includes risk analysis, benefit analysis, and control analysis. As previously indicated, all these areas are being researched for EPA by CARCE.

Prior to 1977, EPA derived its authority to control chlorofluorocarbons (CFC's) from the Toxic Substances Control Act (TSCA). The rationale was that, while CFC's may not in themselves be toxic, they lead to stratospheric O_3 depletion, increased amounts of UV radiation falling on the earth's surface, and, in turn, an increase in skin cancer.

BIOLOGICAL AND CLIMATIC EFFECTS RESEARCH PROGRAM

In Fiscal Year 1976 (FY-76) and FY-77, EPA initiated a short-term $4,000,000 Biological and Climatic Effects Research (BACER) Program to provide the scientific information needed for a decision on whether or not to regulate nonessential uses of CFC's (e.g., as aerosol propellants).

In 1978, because of a number of serious budget cuts, the total funding available from various sources was ~$1,000,000. In the present FY-79, the budget is ~$1,170,000; perhaps $1,400,000 will be allotted in FY-80. Due to this low level of funding, all areas and projects cannot be maintained at an optimum level.

Table 5-1 shows the categorical expenditures of BACER for FY-76 and FY-77; Figure 5-3 shows the agencies that performed the research. The U.S. Department of Agriculture (USDA) received nearly $1,000,000: ~$750,000 to study the effects of O_3 depletion on plants, a much smaller amount to study effects on animals, and $150,000 for instrumentation to measure UV radiation. NOAA received ~$700,000; NASA, less than $50,000. Within a budget of ~$700,000, the National Cancer Institute (NCI) performed skin cancer surveys and studied UV radiation exposure as a function of life-style. EPA is trying to reduce uncertainty in estimates of exposure to UV radiation by developing a miniaturized, personal dosimeter that a volunteer can wear. This electronic device will have the ability to read while retaining its memory, to permit weekly and monthly readouts of the wearer's actual exposure to UV-B.

TABLE 5-1. BACER EXPENDITURES BY CATEGORY FOR FY-76 AND FY-77

Category	Allocation (dollars)
Program Management	450,000
Data Analysis, Policy Analysis, and Report Preparation	537,000
Climate and UV Monitoring	438,000
Terrestrial Ecosystem Effects	800,000
Aquatics Ecosystem Effects	445,000
Human Health Effects	740,000
Economics Analysis	200,000
Instrumentation	390,000
	4,000,000

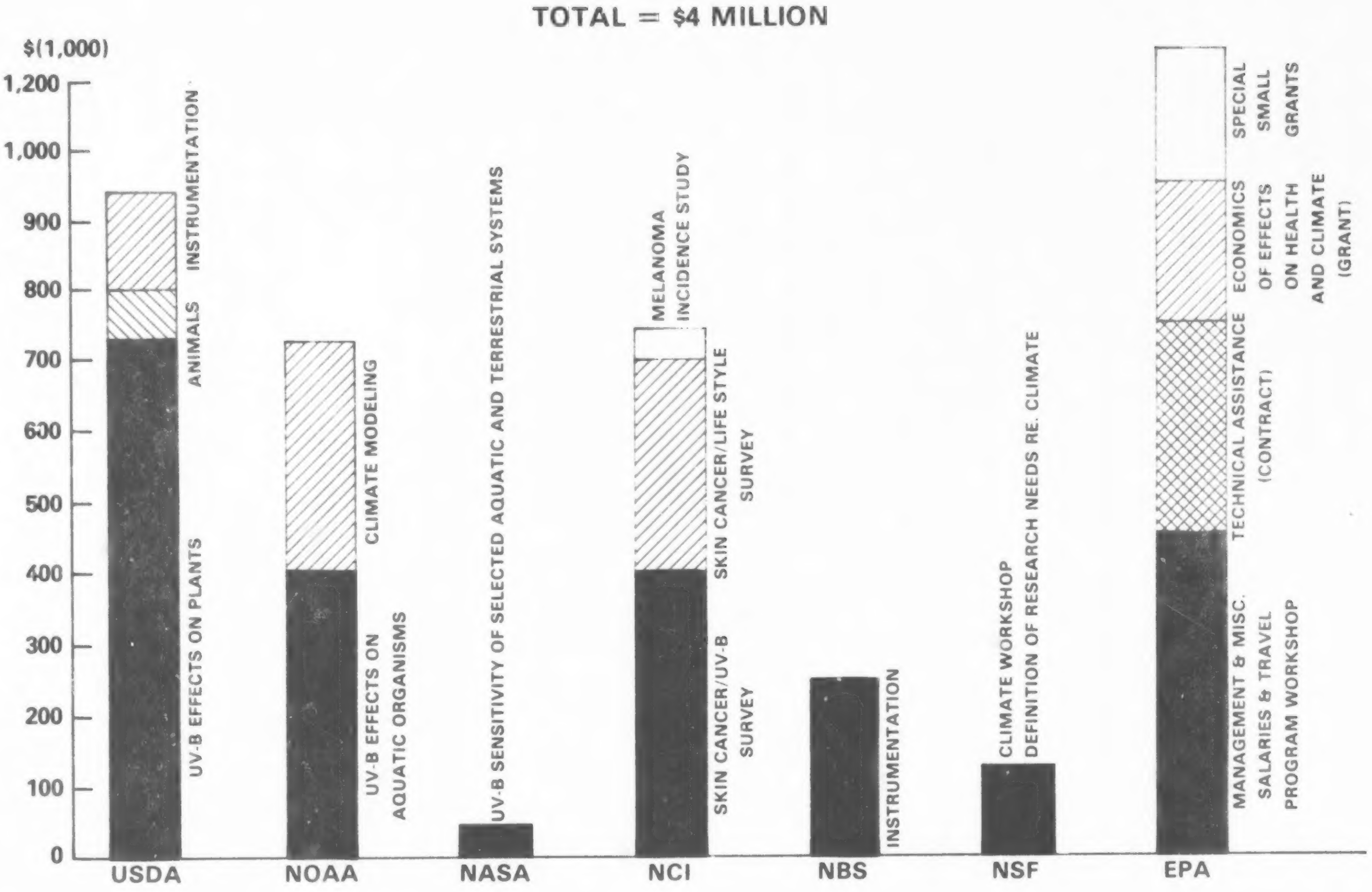


Figure 5-3. BACER budget by agency for FY-77.

The National Bureau of Standards (NBS) developed standard reference lamps and procedures for calibration of instruments; the National Science Foundation (NSF) managed a workshop and produced a report on climatic effects of O_3 depletion.

The EPA expenditures of $1,245,000 covered several years of staff expenses, plus a technical support contract with SRI International to help produce a report to Congress which considered socioeconomic effects. Some special small grants were also included in this amount.

In FY-78, funds were so low that most existing programs were kept alive by token support. NOAA received $110,000 to study the penetration of UV-B radiation into natural waters and consequent effects on aquatic organisms. Of this amount, $39,000 was to study UV-B effects on eggs and larvae of anchovy; anchovies are very important commercially as an additive to chicken feed, and are necessary to the food chain of many larger marine organisms (fish). It was only just possible to keep the Robertson-Berger Sunburn Meter Network functional for $25,000, but support has been increased to $100,000 for FY-79.

Of $400,000 contributed to EPA by OTS, $275,000 was used in partial payment of a contract with NAS to support the two committees mentioned above. OTS money originally intended for ICSOP and interdisciplinary workshop support was diverted into a grant for the University of Maryland to research possibilities of international controls, which are presently of great interest to EPA. No standardization or calibration work was supported; however, the University of Lowell received a grant of $50,000 for instrumentation to monitor solar UV-B radiation.

NCI contributed a small amount of money for three studies: UV-B-induced photooxidation in skin; UV-A and UV-B effects on skin of mice; and monitoring of UV-B irradiance received by humans. In the second of these three studies, previous exposure to UV-A (wavelengths between 320 and 400 nm) was found to sensitize the skin and make it more sensitive to UV-B. This was an unexpected finding; for many years, no danger at all had been associated with UV-A. The results from this Emory University study will be published in the summer of 1979.

STRATOSPHERIC IMPACT RESEARCH AND ASSESSMENT PROGRAM

In FY-79, the name of BACER was changed to Stratospheric Impact Research and Assessment (SIRA), to better indicate the broadened responsibilities of EPA under the Clean Air Act Amendments of 1977. An outline of SIRA is given below.

To begin with, EPA is spending a small amount of money at the University of Utah to study UV-B and UV-A radiation effects on selected plants. In the future, funds will be allocated for examination of crop yield and photorepair, and for a 3-year study of commercially important crops using four plots under very carefully controlled conditions.

A second research area involves a small allocation for an exploratory study of UV-B effects on photosynthesis. As yet, no grant has been awarded for this study, although EPA has contacted many of the nation's top experts. To produce meaningful information will probably require a long-term research program.

Two further areas of research are the previously mentioned studies of UV-B effects on eggs and larvae of anchovy, and on zooplankton. Considerably more work is needed to establish and quantify these effects.

Funding for the Robertson-Berger Sunburn Meter Network has been restored to the $100,000 level. This new funding level will allow greater collection and analysis of UV-B incidence data.

In the area of quality control, ~$125,000 is available for instrument calibration purposes, and ~$100,000 is available for spectrally resolved monitoring of UV-B incidence. The means by which this work will be accomplished are as yet undetermined.

Ongoing research strives to improve the correlation of skin cancer with UV-B exposure, but funding is not available for all work areas. A solution to limited funding may be to purchase 600 personal dosimeters (~$60,000) and to conduct a survey with 600 volunteers (~$30,000). An alternative being explored is to purchase small quantities of the currently available UV-B-sensitive strips (samples might be obtained for ~$5,000) for comparison in a laboratory with the miniature dosimeters. The 6 prototype dosimeters that EPA will receive under the present grant will also be compared with film strips, in the field, by people wearing both types. It may be desirable to use the 6 prototype dosimeters as reference standards and proceed with film strips on 10,000 subjects. The cost difference in using 600 dosimeters or 10,000 sets of film strips is minimal, so the method used will depend on the results of preliminary studies.

The next area of research involves the relationship of UV-B to erythema, melanoma, and nonmelanoma. This is, of course, a topic of great interest. Though only small amounts of funds have been allocated, the studies are continuations of ongoing work. Dr. Elizabeth Scott of the University of California at Berkeley is analyzing data collected by the National Center for Health Statistics (NCHS) for three specific areas: (1) mortality by site of lesion on the body, separately for melanoma and nonmelanoma, (2) cases of skin cancer and of various keratoses obtained in the NCHS Health and Nutrition Examination Survey, and (3) cases of skin cancer, separately for melanoma and nonmelanoma, observed by a NCHS sample of discharges from short-stay hospital care.

Using previously available data and unpublished data from NCHS tapes for the period 1950-1974, Dr. John Lee of the University of Washington at Seattle is developing age-specific mortality rates, by sex and race, for malignant melanoma, other primary skin cancers, and total primary skin cancer. Through these research programs, EPA hopes to create a model for forecasting increases in melanoma and nonmelanoma cancers from UV-B enhancement.

As indicated earlier, EPA is the only agency designated to carry out a complete, integrated assessment of the entire range of causes, effects, and controls of O_3 depletion. EPA already has funded a contract for undertaking a complete integrated assessment, the product of which will be used to prepare the required 1980 biennial report to Congress. A grant for socioeconomic analyses has produced state-of-the-art cost-benefit studies. In addition, several areas where additional studies will reduce uncertainties have been identified. These include the development of systematic measures of damage that are compatible with measures of regulation cost. Econometric extensions to epidemiological studies as well as improved sensitivity analyses of health, ecological, and climatic damage estimates will also be undertaken. The global nature of the O_3 problem, and the difficulty of dealing with risk when the possibility of irreversible damage is present, are recognized to require particular conceptual and analytic attention.

The mandated NAS study of the state of knowledge and adequacy of research on causes, effects, and controls of stratospheric O_3 depletion is being supported. NAS has scheduled delivery of its report for fall 1979. Funding is again limited; to ease the financial burden, EPA has persuaded NAS to receive the money in installments of $270,000 and $85,000.

In the final area, program management, costs have been cut to $125,000.

EFFECTS OF UV-B RADIATION

This report concludes with illustrations indicating the effects of UV-B. Figure 5-4 shows a small instrument developed by USDA to measure the radiation incident on plants. It can be substituted for one of the exposure pots. The meter is coupled to the computer seen on the tray that will integrate the required spectrally-resolved data.

Figure 5-5 shows effects of UV-B on cucumber plants. The plant on the left was protected from UV-B by Mylar, which passes virtually no UV radiation in the UV-B region; the middle plant experienced a 50-percent increase over the amount it would naturally encounter; and the plant on the right was subjected to a 200-percent increase. It is very interesting that the 50-percent increase in UV-B exposure had a significant effect on the middle plant's growth, because a plant taken from the natural environment (i.e., the field) and protected from solar radiation with Mylar will actually grow taller. UV-B may thus act as a natural growth controller for plants; determining the extent

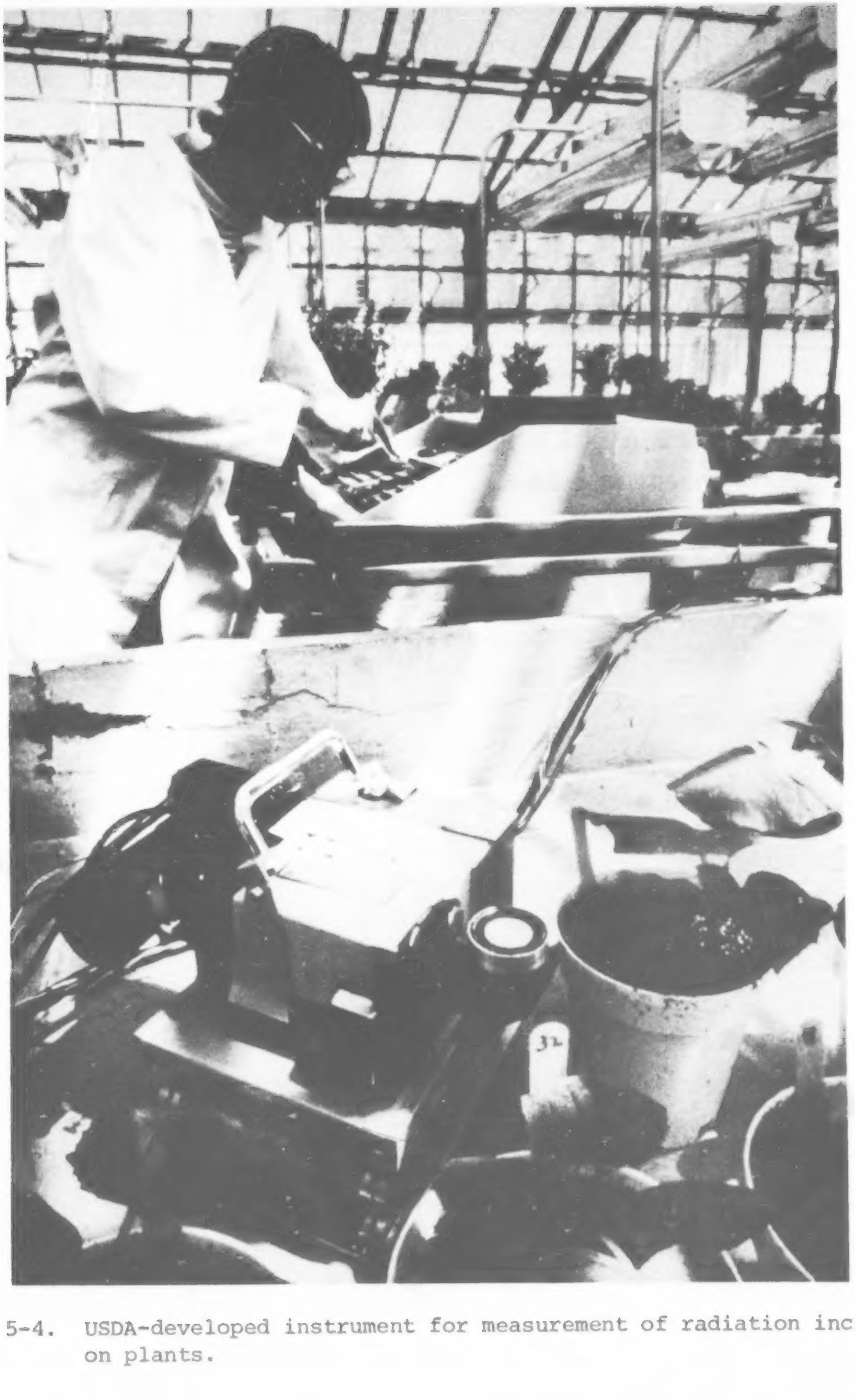


Figure 5-4. USDA-developed instrument for measurement of radiation incident on plants.

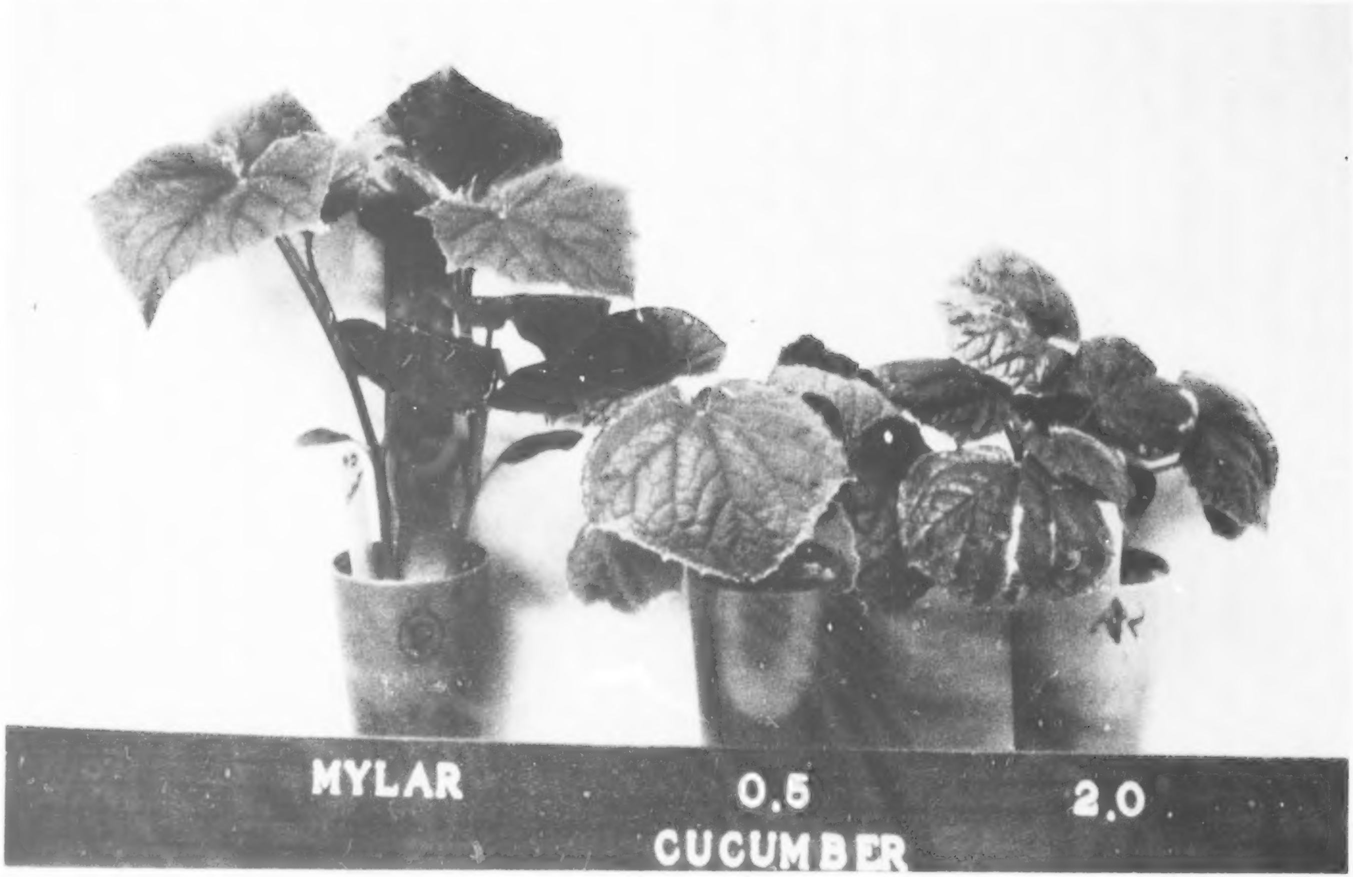

MYLAR
0.5
2.0
CUCUMBER

Figure 5-5. Effects of UV-B on cucumber plants.

of such an effect is crucial. Increases in UV-B exposure of >50 percent did not seem to have too much additional effect; the plant on the right, which received a 200-percent increase, actually appears slightly healthier than the one exposed to a 50-percent increase. Of course, conclusions cannot be drawn from merely one plant species. The particular species photographed may simply be able to develop an effective repair mechanism. To obtain conclusive results, EPA plans to conduct a 3-year study using several carefully selected plants.

Figure 5-6 is reproduced from an NAS report to show the correlation between areas of UV-B exposure and sites of skin cancer on the human body. On the male figure, the area the swimsuit would cover is virtually free from skin cancer sites, whereas normally exposed areas are covered with such sites. Upon close inspection of the female figure, a peculiar effect is noticeable: the left leg has more skin cancer incidence than the right. The explanation for this is unknown. In any case, changing life-styles are causing incidence of skin cancer in "new" sites on the human body, further suggesting the need for dosimeters to measure actual radiation at particular points of the body.

Figure 5-7 shows the rapidly rising trends of melanoma skin cancer. Are such trends simply due to a change in life-style? One must consider that changes in life-style can actually invert latitude correlations with skin cancer, because life-style can be more important than where a person happens to live. Generally, though, life-style is affected by latitude; i.e., if an individual lives in the South, he is more likely to be outdoors.

More specifically, inhabitants of northern latitudes (e.g., Norway or Sweden) that habitually vacation in the Riviera have been known to later develop skin cancer, whereas their neighbors who stay at home do not. Such "vacationers" have received heavy exposure to UV-B without allowing their bodies to become accustomed; they become very sick. The skin burns and heals very slowly, and eventually skin cancer may develop.

When attempting a correlation, then, a scientist must know where an individual spends his time. A short, intense exposure to UV radiation is more

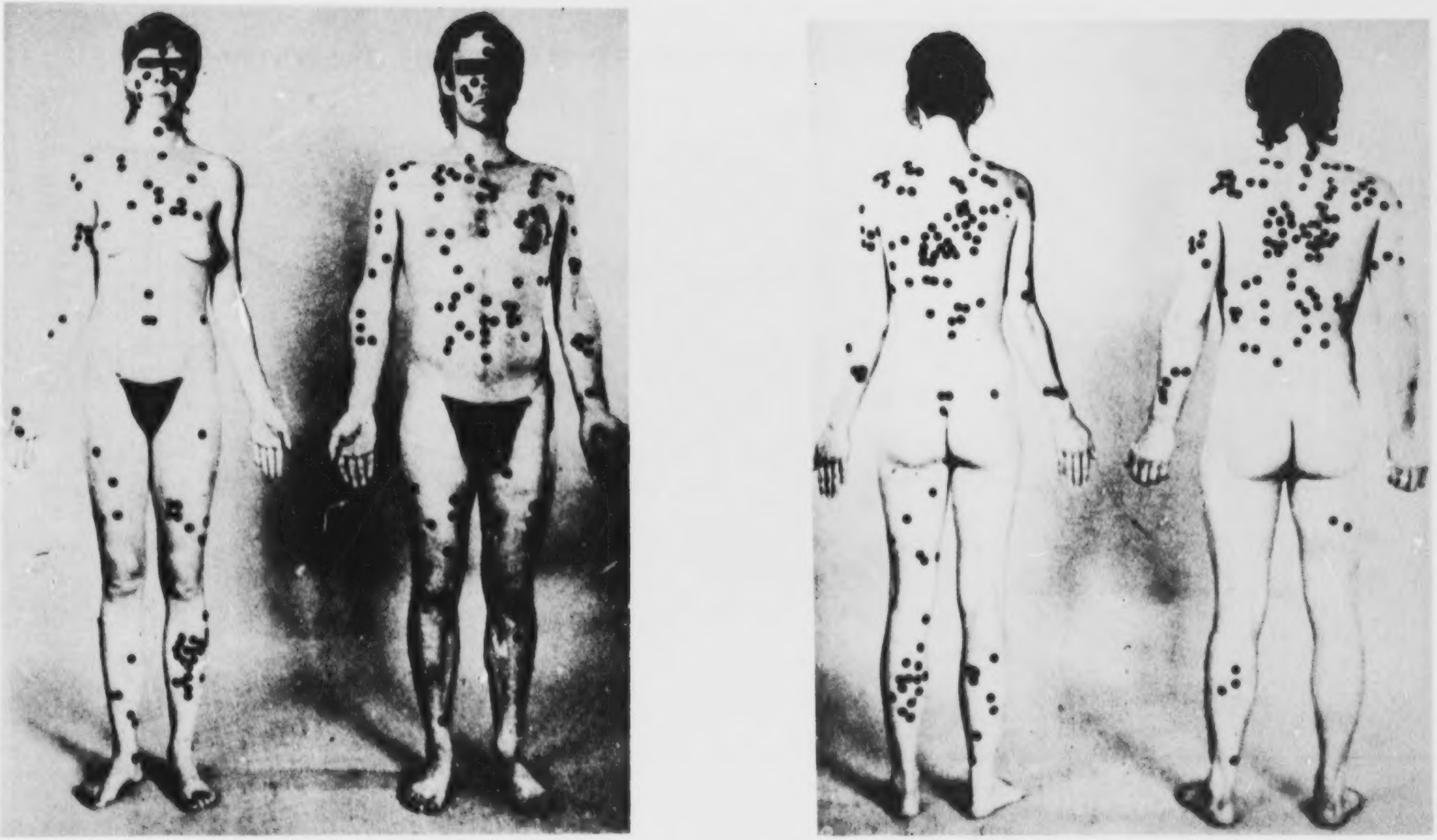
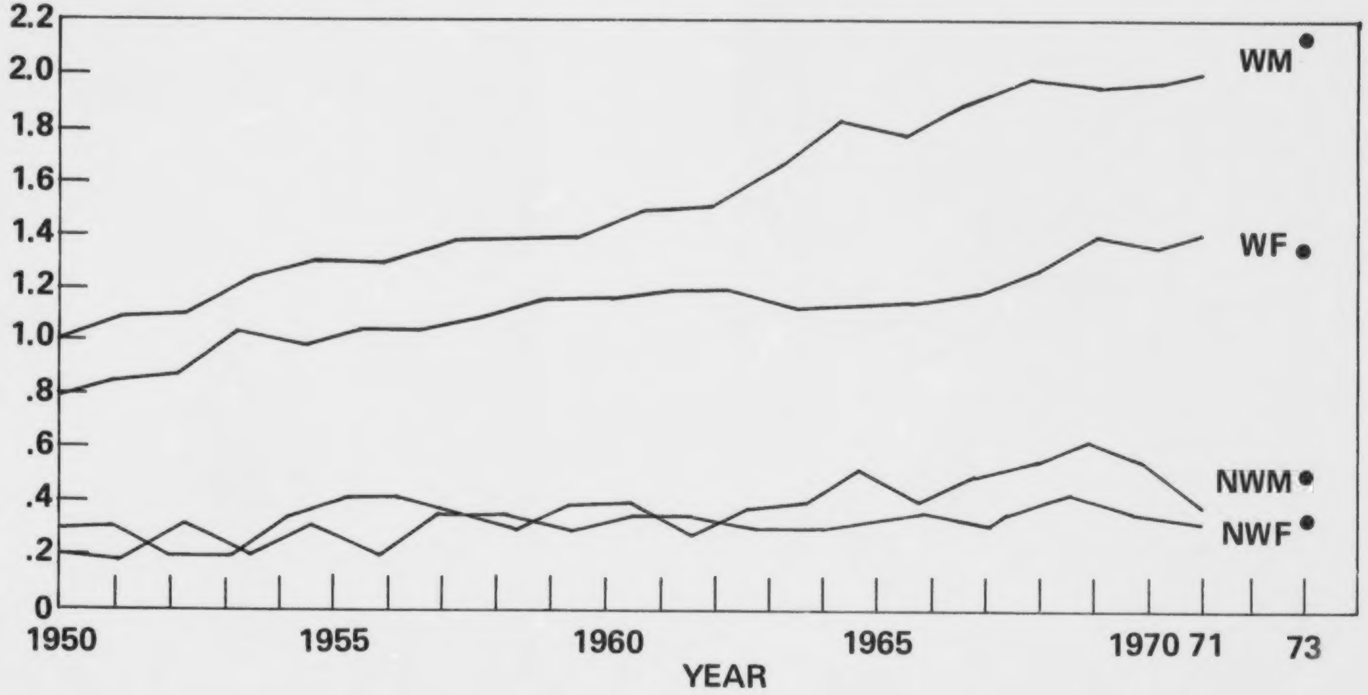


Figure 5-6. Correlation in humans between areas of UV-B exposure and sites of skin cancer.



*AGE-ADJUSTED (1960 US) RATE PER 100,000 POP.

Figure 5-7. Trends in mortality from melanoma of the skin in the U.S., 1950-1970.

A TWO-DIMENSIONAL PHOTOCHEMICAL MODEL TO ESTIMATE STRATOSPHERIC OZONE DEPLETION

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INTRODUCTION

This paper presents some of the first results obtained using a two-dimensional time-dependent photochemical model of the atmosphere, applicable up to 55 km, and incorporating chloride chemistry. The methodology of the model's development has been described previously (Crutzen 1976); the numerical results presented here have been achieved through a refinement combining the chemistry described in a one-dimensional model (Crutzen et al. 1978) and the transport parameterization utilized in the two-dimensional model (Crutzen 1976). Although the results are preliminary, future reductions of ozone (O_3) predicted by this model are consistent with current predictions of one-dimensional models.

RESULTS AND DISCUSSION

Figure 6-1 depicts the model-derived total O_3 distribution as a function of latitude and month. In general, the features agree with the observed total O_3 distribution (Dütsch 1971) shown in Figure 6-2. The major qualitative discrepancy between Figures 6-1 and 6-2 occurs during the Southern Hemisphere (SH) summer near the pole. Quantitatively, the O_3 distribution analyzed by Lovill et al. (1978) using June data from satellite observations yields an average O_3 column density of 296 Dobson Units (DU). The calculated June 1970

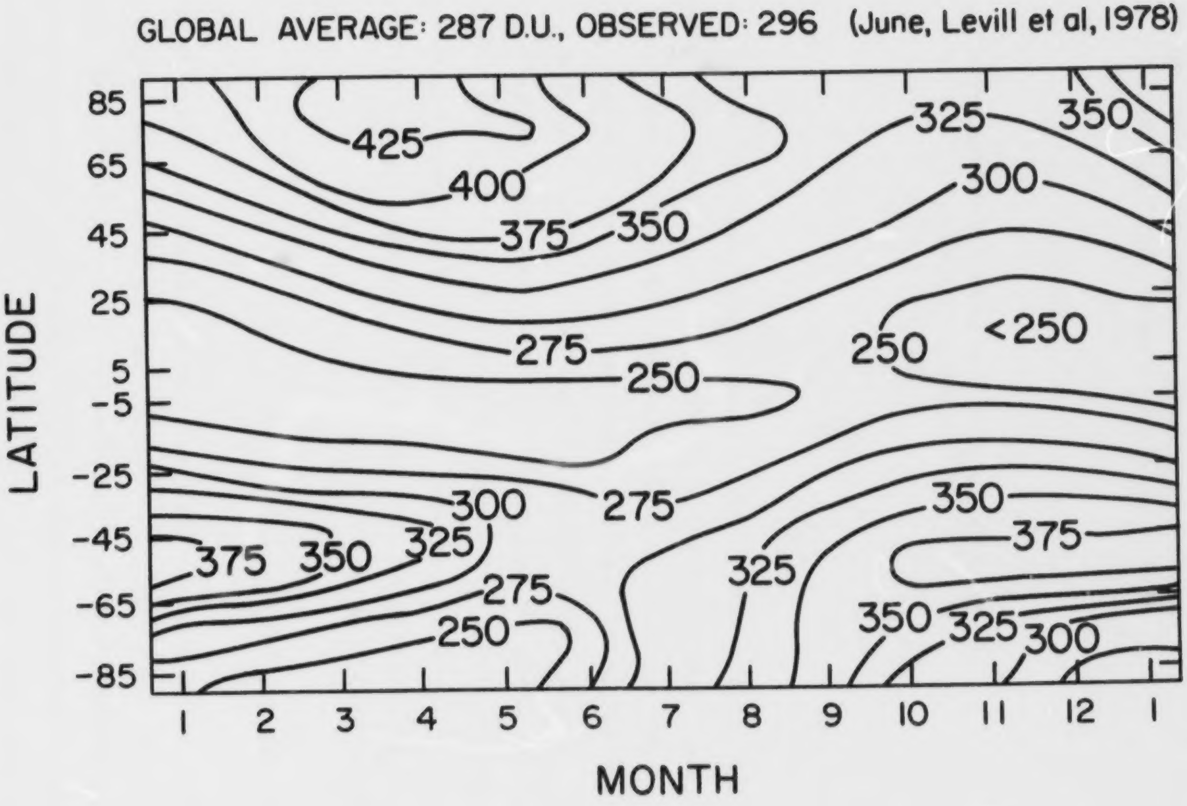

Figure 6-1. Model-derived total O_3 field for 1970 plotted as a function of month and latitude. Contours are in DU.

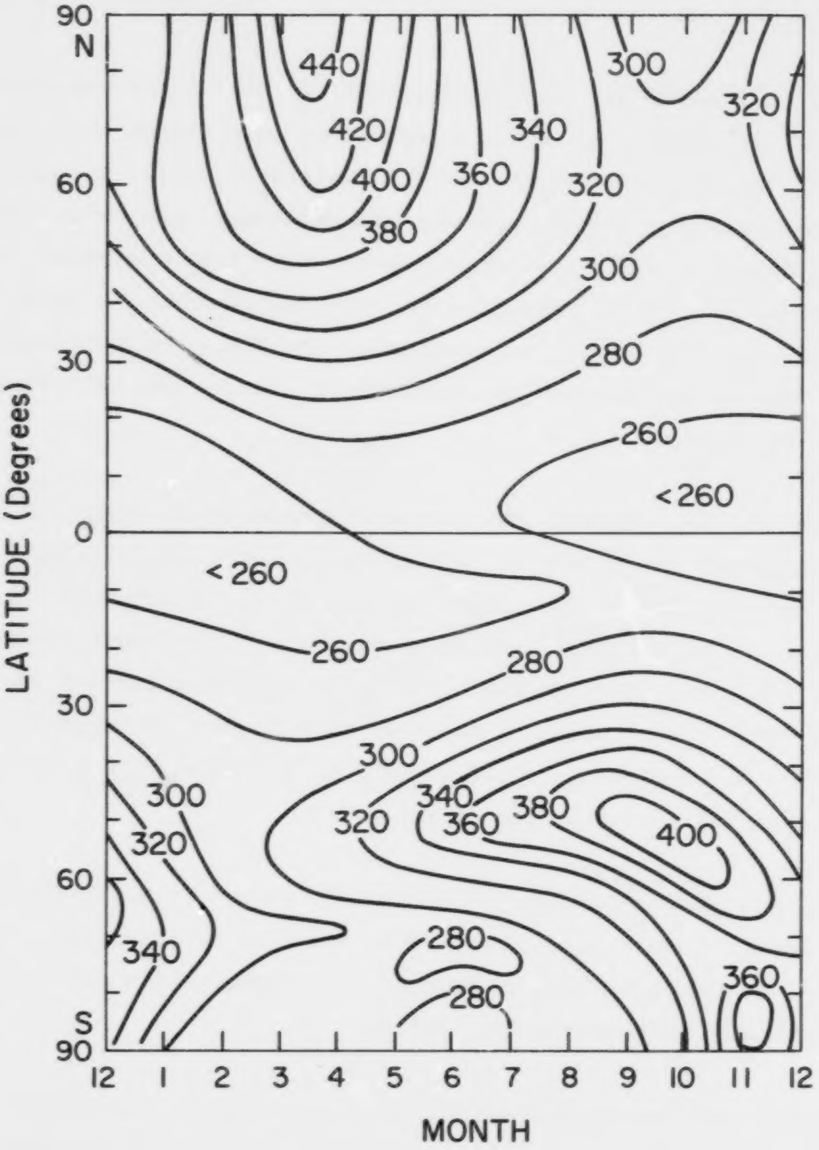

Figure 6-2. Observed total O_3 field plotted as a function of month and latitude. Contours are in DU. Taken from Dütsch 1971.

O_3 distribution yields an average value of 287 DU. The results shown in Figure 6-1 are integrated by the model to 1970 after starting with initial-guess fields in 1960. After 10 yr of numerical integration, the model should have reached equilibrium and should not be affected by the initial fields. The purpose here is to present the calculated O_3 reduction to the year 2001.

Figure 6-3 shows the calculated amount of total O_3 in the atmosphere between 1970 and 2001. The average rate of O_3 loss during this time is 0.24 percent/yr, yielding a total loss of 7.5 percent by 2001. The most recent calculations, using a one-dimensional time-dependent model with comparable chemistry, predict nearly a 5 percent decrease by 1988 (personal communication); the results of the present model similarly indicate a global O_3 loss rate of 5 percent by 1988. The calculations of the one-dimensional model reach an equilibrium loss due to fluorocarbon release (at 1975 release rates) of nearly 19 percent.

Figure 6-3 also depicts the estimated amount of O_3 depletion due to release of methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF) in the contrast between Curve A (continued release of fluorocarbon-11 (trichlorofluoromethane, CCl_3F, FC-11) and fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2, FC-12) at 1975 rates and MCF at 1978 rate) and Curve B (no release of MCF after 1978). The future O_3 loss due to MCF after 14 yr of integration (1978-1992) is 0.9 percent, or 23 percent of the total O_3 depletion computed by the model during this period of integration.

Lastly, Figure 6-3 shows the rate of O_3 depletion in the final year of integration to be ~0.2 percent/yr. This value is somewhat less than the 0.3 percent/yr in the early 1980's; however, the higher values in the early 1980's may be artifacts of model initialization.

Using a two-dimensional model, it is possible to distinguish latitudes and seasons of greatest O_3 depletion. Although the 30-yr integration (1970 to 2000) yields an average O_3 depletion of 0.24 percent/yr, examination of Figure 6-4 indicates that this depletion rate is not constant with latitude. More O_3 is destroyed at high latitudes than in the tropics; the highest loss

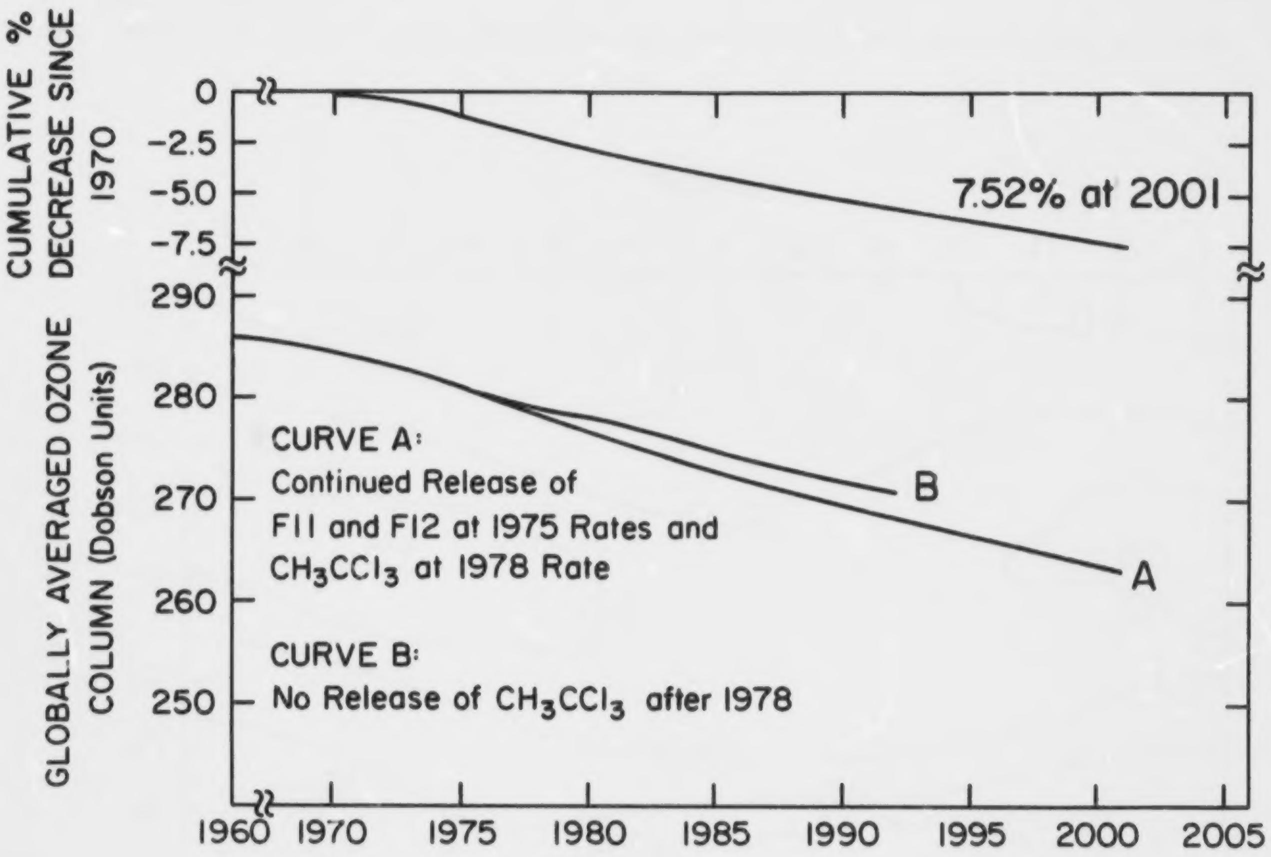

Figure 6-3. Model calculations of depletion of global O_3. Top curve depicts the cumulative loss from 1970 to 2001 (in percent); Curve A is the average column density of O_3 (in DU) calculated using current release rates for the fluorocarbons and MCF; Curve B is the same as Curve A except that no O_3 loss is permitted in the calculations to occur by release of MCF after 1978.

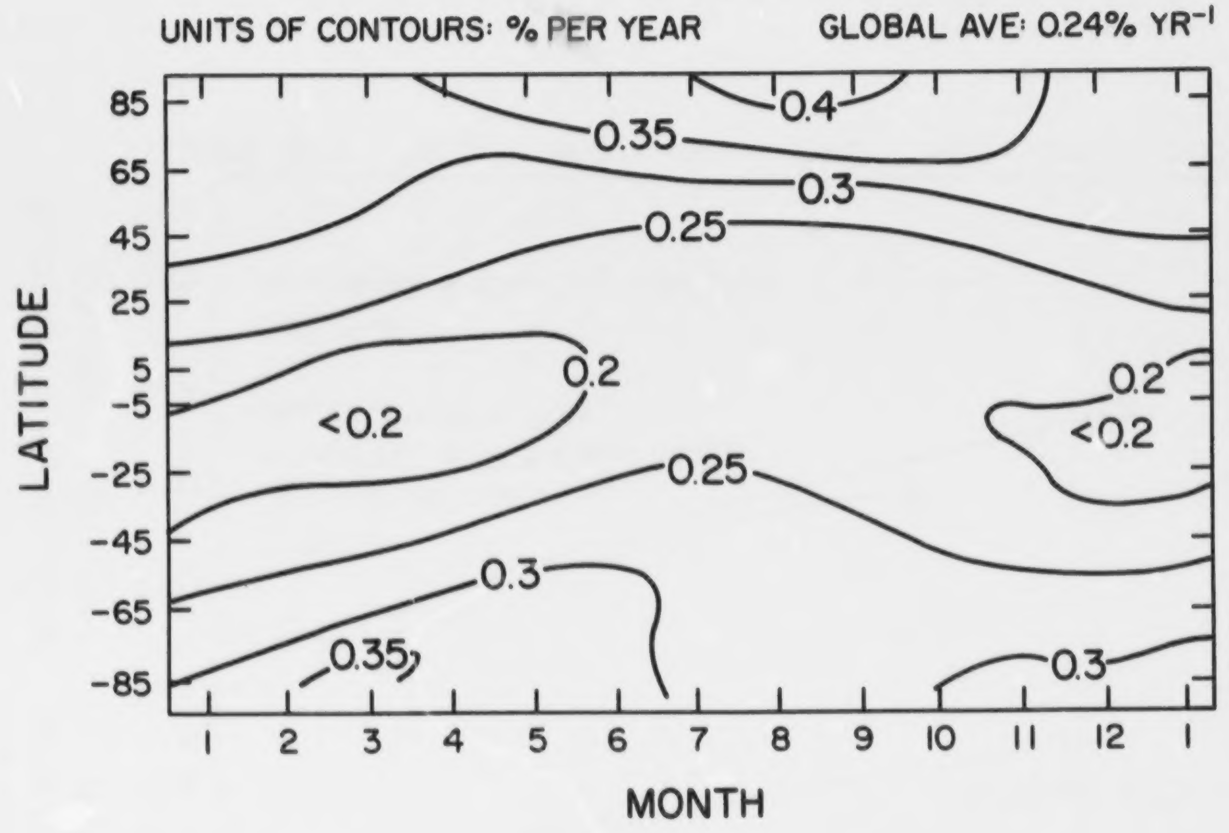

Figure 6-4. Month and latitude distribution of average total O_3 loss between 1970 and 2000. Units are percent/yr.

rate is seen during the summer season at north polar latitudes. Similarly, an enhancement of the O_3 loss rate is seen at SH middle and high latitudes during the summer season.

Figure 6-5 reveals that the rate of O_3 loss varies with altitude and latitude. The highest loss rate occurs in the tropics near an altitude of 40 km. The cumulative loss rate at this level is 25 percent (0.8 percent/yr). This result is consistent with that from a one-dimensional model (Crutzen et al. 1978), where the greatest loss rate centered near an altitude of 40 km. This finding appears to contradict Figure 6-4, which suggests that less O_3 depletion occurs in the tropics. Figure 6-6 helps to clarify these seemingly contradictory statements.

Figure 6-6 is the winter O_3 concentration calculated by the model. The contours, in units of molecules/cm^3, illustrate that the O_3 concentration is only ~5 x 10^{11} mol/cm^3 in the region having the highest percentage of O_3 depletion. This concentration is about a factor of 10 lower than the regions of maximum O_3 concentration: 20 to 25 km at middle and high latitudes. Thus, a high depletion rate at an altitude of 40 km does not cause as strong a depletion in the total O_3 column as a more moderate depletion rate in regions where O_3 concentrations are significantly higher.

AREAS FOR IMPROVEMENT

Ongoing refinements to the model will permit a better representation of the distribution of trace gases. Major deficiencies of the current model include the calculation of too small O_3 concentrations in the tropical troposphere and too large interhemispheric gradients for the chlorocarbon compounds. Both findings suggest that horizontal transport processes between the hemispheres are too small. The fact that calculated O_3 and nitrogen oxides (NO_x) concentrations in the tropical troposphere are smaller than observed values likewise suggests that an important NO_x source term is missing in this region.

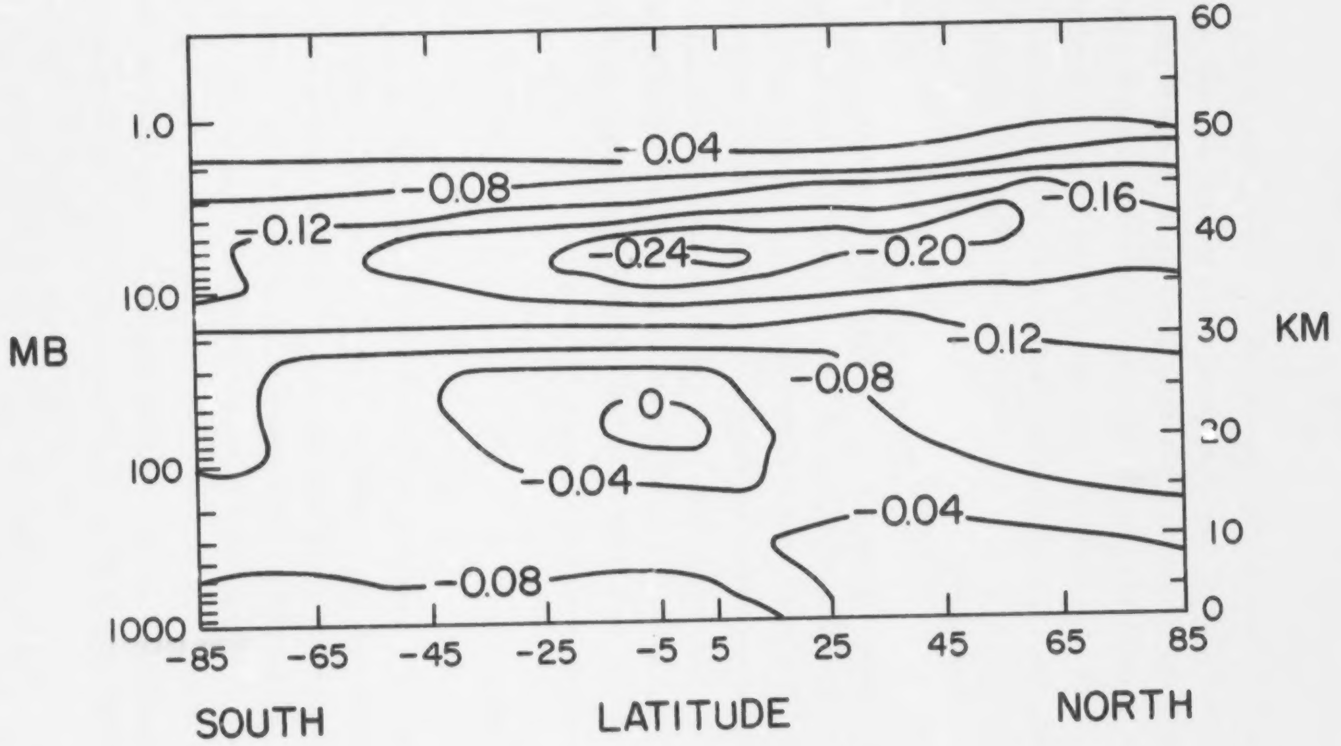

Figure 6-5. Latitude and altitude distribution of cumulative O_3 loss after 10 yr of model integration. Units are dimensionless and represent the fraction of O_3 lost at a given location (e.g., -0.20 refers to the contour where 2 percent of O_3 has been depleted).

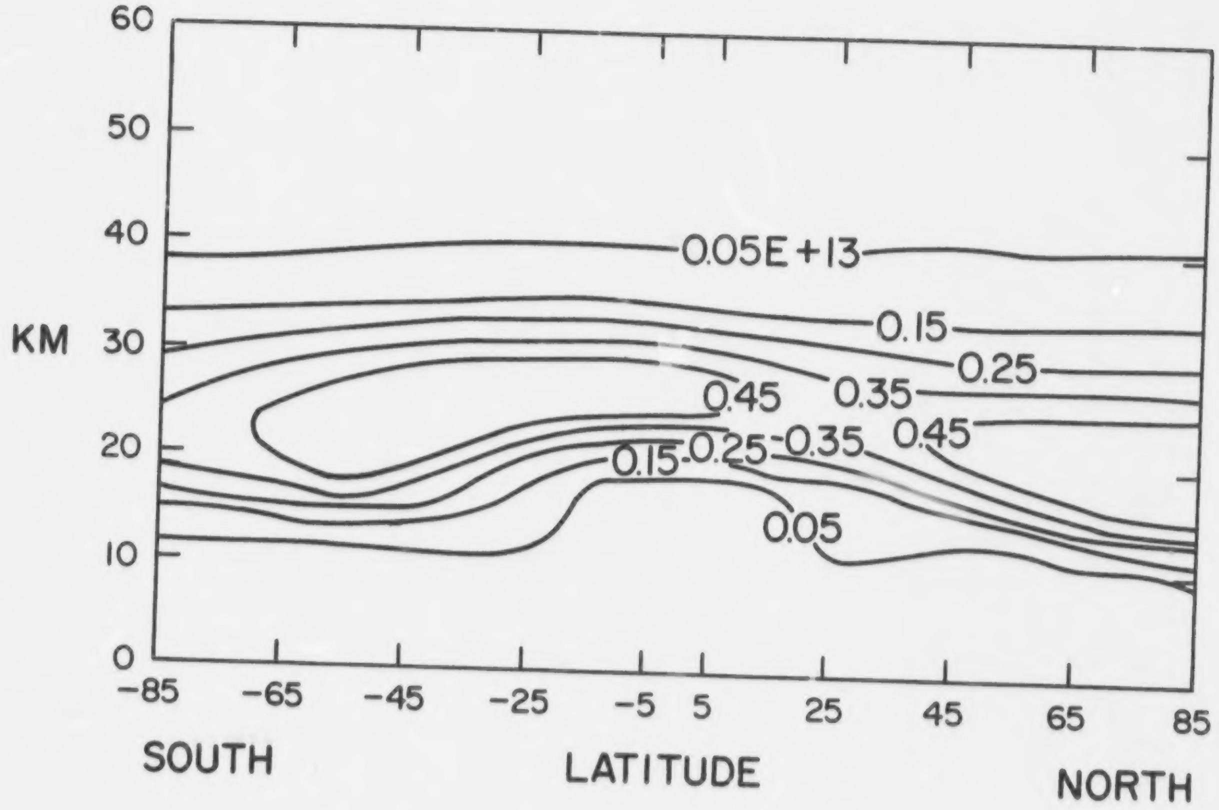

Figure 6-6. Model-derived distribution of O_3 for December 1970. Units are molecules/cm^3.

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DISCUSSION

Dr. Hanst: Someone mentioned a 3 ppb figure for tropospheric Cl, accounting for all halocarbon contributions; also, significant chlorine monoxide radical (ClO) and hydrochloric acid (HCl) concentrations occur in the stratosphere. Has total Cl as a function of altitude been plotted, and are there discontinuities?

Dr. Crutzen: In the one-dimensional model, there are never any discontinuities. Obviously, a total stratospheric Cl measurement is also needed. Walter Berg, who is with my group, has done this; the measurements were made at 20 to 25 km. The data are being analyzed, and will be reported in the near future.

Voice from Audience: Do you have a number from your model for the stratospheric O_3 exchange or O_3 flux from the stratosphere into the tropozone?

Dr. Crutzen: No, I don't have a number; it is calculated and in my data sheets. The number is ~5×10^{10} molecules/cm^2/s, close to the destruction rate at the ground. It's quite mysterious, because I believe a great amount of O_3 is created and destroyed in the troposphere. Maybe all these interactions produce a balancing effect. Actually, it is difficult to make these estimates because of the tropospheric nitric oxide (NO) uncertainties.

Dr. Schiff: Your current modeling figure is an average 0.5 percent/yr depletion [a better answer is supplied in the preceding report]. Does that mean the amount of O_3 loss due to the Cl from FC-11, FC-12, and MCF is 0.5 percent?

Dr. Crutzen: It approaches 0.5 percent, yes.

Dr. Schiff: A second question concerns tropical O_3. In your model, when you are at 0° latitude, what do you use for NO? What is your boundary condition?

Dr. Crutzen: For tropical O_3 at low altitudes, I consider only one input of NO, the industrial source at mid-latitudes. The NO diffuses, nitric acid (HNO_3) is produced, and it is rained out with a certain scheme. According to this pattern, hardly any NO_x reaches the tropics; however, additional possible sources for NO_x exist in the tropics. One of them is lightning. We estimate between 0 and 40 megatons/yr, so that is a major problem in the tropical regions. But I am quite certain that local O_3 formation in the tropics is taking place. It's a slow process, but it is just necessary to maintain the O_3 at average reported levels.

Voice from Audience: From that model, do you have an integrated estimate of the O_3 lost from 1950 to 1977?

Dr. Crutzen: The number is around 1.5 or 2 percent, but I must refer to the data.

Voice from Audience: I think the discontinuity is repeated. You are quoting one-dimensional models for the past to the present and two-dimensional models for future estimates.

Dr. Crutzen: I'm speaking from memory regarding the one-dimensional model, but I'm using the good reasonable agreement between results of the two-dimensional and one-dimensional models.

A REVIEW OF TECHNICAL PROGRAMS
OF THE MANUFACTURING CHEMISTS ASSOCIATION
RELATED TO STRATOSPHERIC CHEMISTRY OF CHLORINE

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INTRODUCTION

Calculations of stratospheric ozone (O_3) depletion by chlorine (Cl) rest on a number of assumptions, most of which are subject to direct test. A final conclusion based on such calculations can also be tested by direct measurement in the stratosphere. Three of the basic assumptions are:

(1) Chlorofluorocarbons (CFC's) are not destroyed in the lower atmosphere, but are transported quantitatively to the stratosphere.

(2) All stratospheric processes involving Cl are known.

(3) Reaction rates under stratospheric conditions are known with sufficient accuracy to make reliable predictions.

This paper discusses measurement programs directed to clarifying these assumptions and examines O_3 trend analysis, which constitutes a direct test of predicted O_3 depletion.

ATMOSPHERIC LIFETIME

A relevant question is whether significant removal processes exist in the troposphere for halogenated organic compounds. Techniques developed to identify any occurring sink mechanisms are directly applicable to determining the lifetime of a species for which accurate release data can be developed.

Most atmospheric model studies assume that chlorofluoromethanes (CFM's) are transported quantitatively from the surface to the stratosphere, or (equivalently) that tropospheric lifetime is very long. A tropospheric lifetime of 100 or 300 yr is usually assumed.

The relative importance of tropospheric sinks reducing the amounts of Cl transported to the stratosphere was evaluated in 1976 by the National Academy of Sciences (NAS). Removal by oceans was determined to be the only potentially significant sink. The existence of undiscovered sinks and the quantification of all sinks are of considerable importance, since tropospheric lifetime depends on the additive effect of many removal processes.

Recently, fully halogenated compounds — carbon tetrachloride (CCl_4), fluorocarbon-11 (trichlorofluoromethane, CCl_3F, FC-11), and fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2, FC-12) — have been shown to undergo a heterogeneous reaction on certain mineral dust surfaces. Several investigators have observed FC-12 during analysis of tropospheric air, but since its industrial production is very small and its tropospheric lifetime should be relatively short, any concentration should fall well below measurable levels. If the occurrence of FC-12 is firmly established, the most probable source is conversion of FC-11. Reduction of FC-11 is known to occur in biological systems (Cox et al. 1976; Wolf et al. 1975) and in such applications as refrigeration and foam-blowing agents.

Early attempts to identify possible removal mechanisms for CFM's were based on calculations of global burdens from a few localized measurements in the lower atmosphere and on approximations of fluorocarbon release. Uncertainties associated with these measurements, such as variability of the atmosphere, inherent errors in any analytical method, and possible uncertainties in calibration, are too large to inspire confidence in the final calculation of the global burden. In fact, the quality of the measurements permits only a conclusion that the tropospheric lifetimes of CFM's are between 10 and ∞ yr. Work supported by the Manufacturing Chemists Association (MCA) Technical Panel has removed many uncertainties connected with the analytical method and with world production and release of fluorocarbons.

Rigorous procedures for analysis of FC-11 and FC-12 have reduced analytical errors to <2 percent. Absolute standards can now be made for calibrating the chromatographs. With these standards, Lovelock (private communication to MCA 1978) has shown that absolute coulometry, properly applied, is valid within ~7 percent. But the persistent uncertainties in determining global burden due to natural variability of the atmosphere can be resolved by an alternate approach.

The Technical Panel is supporting a measurement study, the Atmospheric Lifetime Experiment, to determine directly the lifetime of CFM's in the atmosphere. A method developed by Cunnold et al. (1978) involves global-scale determination of tropospheric concentration trends of CFM's by frequent measurement at stations strategically located worldwide. Stations located at Adrigole (Ireland), Barbados (off the northeast coast of South America), American Samoa (in the mid-Pacific), and Cape Grim, Tasmania (off the southeast coast of Australia) make hourly measurements of FC-11 and FC-12, nitrous oxide (N_2O), CCl_4, and methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF). Measurements of other species are made when the investigators visit the stations for routine servicing. After a global trend is established by measurement, it is compared to the expected trend derived from release statistics provided by member companies of the MCA Technical Panel. A statistically significant difference in slope of the two trend lines would indicate the existence of a removal mechanism operating in the atmosphere, or a natural source of CFC's.

Cunnold et al. (1978) estimate that a 10-yr lifetime can be detected within 3 yr of measurement, and that a 20-yr lifetime can be detected within ~5 yr. The stations have been in full operation since the second quarter of 1978, and the first year's data will soon be processed.

STRATOSPHERIC MEASUREMENT

Approximately 100 chemical reactions are significant to stratospheric Cl chemistry. This discussion will concentrate on the catalytic O_3 depletion cycle:

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \\ \underline{ClO + O \rightarrow Cl + O_2} \\ \quad O + O_3 \rightarrow 2O_2 \end{array} \qquad \text{(Eq. 1)}$$

as postulated by Stolarski and Cicerone (1974), Cicerone (1974), and Wofsy and McElroy (1974). The measurement of chlorine monoxide radical (ClO) and other Cl species in the stratosphere was quickly recognized as one direct test of the O_3 depletion hypothesis.

In 1975, the Technical Panel supported the development of an analytical method for ClO based on the following reaction (Stedman et al. 1975):

$$ClO + NO \rightarrow Cl + NO_2 \qquad \text{(Eq. 2)}$$

After conversion of the ClO to Cl, the concentration of Cl atoms is determined by resonance fluorescence. This method was applied by Anderson et al. (1977) in a series of stratospheric probes. They observed that the concentration of ClO in the mid-stratosphere follows an apparent seasonal pattern, in which ClO ranges from a low winter value of <1 ppb to a high summer value of ~8 ppb. In September 1978, Menzies (1979) observed ~2 ppb at sunset, which by model calculation is equivalent to ~4 ppb at noon.

One interesting result of these measurements is that the amount of ClO detected is much larger than the amount of total Cl calculated to be present in the stratosphere. Also interesting are the normal O_3 levels observed simultaneously with the highest levels of ClO. According to present calculations, O_3 should be dramatically decreased at such high levels of ClO. If the measurements prove to be valid (no flaws have yet been found), one conclusion to be drawn is that Cl does not deplete stratospheric O_3.

The Technical Panel is continuing its stratospheric measurement effort to develop additional information for understanding more precisely the true chemistry of Cl in the stratosphere. Balloon probes by Murcray (work in progress), Bonetti (work in progress), and Harries (work in progress) are attempting to identify other Cl species that may help to explain the unpredicted behavior of ClO in the stratosphere. Total Cl measurement is one of the most important experiments remaining to be accomplished; the MCA Technical Panel is preparing a flight probe for mid-1979, but the analytical procedures are so difficult that predictions of success are not now possible. Balloon snapshot experiments, most useful for producing simultaneous data on reactive species, are complemented by long-term monitoring. In addition to the balloon probe effort, MCA has established infrared monitoring capability for hydrochloric acid (HCl) and hydrogen fluoride (HF) at Jungfraujoch in Switzerland, microwave monitoring for ClO at the University of Massachusetts in Amherst, and solar scanning at Mt. Evans in Colorado.

REACTION RATES

During the last few years, rate measurements of reactions of many trace species have been refined. Perhaps the most surprising development in kinetics is the discovery that HO_2 reacts with nitric oxide (NO) 30 to 40 times faster than originally believed. The observed rapid reaction between ClO and HO_2 boosts the possible importance of hypochlorous acid (HOCl) in stratospheric chemistry.

The Technical Panel also supports work on determination of absorption cross sections, particularly HOCl; branching ratios of reaction having alternate pathways; and rates for reactions relevant to Cl chemistry. Evaluating the pressure dependence of some of the key reactions is particularly important.

OZONE TREND ANALYSIS

Direct observation of the O_3 layer will provide the final test of depletion calculations. The Technical Panel has funded statistical analyses of O_3 measurements gathered over the past years. The most powerful technique for analysis of data collected over extended periods is a statistical procedure known as time series analysis (Box and Jenkins 1970). Such analysis is capable of detecting abnormal trends that may exist in a long series of variable data. Normal cycles are identified by data analysis and then factored out of the observations. The process is repeated until only random noise, as measured by appropriate statistical tests, remains. Any trend is detected by an upward or downward slope of the random noise line.

Time series analyses have been conducted on Dobson O_3 data by Hill and Sheldon (1975) and Pagano and Parzen (1975). Hill and Sheldon estimate that their analysis of Dobson data would detect a potential change of 0.26 percent/yr persisting for 6 yr (total 1.56 percent). Neither study has found a statistically significant trend during the period 1970 to 1975. This analysis method promises to provide an early warning of any abnormal change in O_3 level.

Since one-dimensional models predict that CFC's have already depleted O_3 by 1.5 to 2 percent, and that MCF has already depleted O_3 by ~0.3 to ~0.5 percent, a total of ~1.8 to ~2.5 percent O_3 depletion should already have occurred. If a trend of this magnitude exists, it should be detectable now, and in 1 to 2 yr the calculated depletion should be well above the detection limit.

Current model calculations indicate that the O_3 layer is most sensitive to perturbation by Cl in the 35 to 45 km region of the stratosphere. In this region, chemical reactions are expected to dominate O_3 concentration; in lower levels, transport phenomena and perturbations from the troposphere are expected to be complicating factors. In the 35 to 45 km region, predictions indicate that depletion by several percent should already exist. Angell and Korshover (1978) have analyzed O_3 data from this region and conclude that the O_3 level over north temperate latitudes increased by perhaps 8 percent between 1962 and 1973.

Present analyses of O_3 data yield no direct evidence for existence of O_3 depletion at this time. But the Technical Panel is supporting additional work in time series analysis of data gathered by the Nimbus satellite. Additional O_3 data from this source may improve sensitivity to trends.

SUMMARY

The question of the existence of significant tropospheric sinks for fluorocarbons is not yet answered, and reliable calculations of O_3 depletion cannot be made without these data. Since recent observations of ClO and O_3 in the stratosphere are not consistent with current models of stratospheric chemistry, the resolution of this discrepancy is vital to deeper understanding of the stratosphere. Continuing refinement of reaction rate data and photodissociation cross sections is desirable, especially as new species are found to be important in stratospheric chemistry.

Careful analysis of available O_3 data does not show a detectable trend in global O_3. Further analysis of existing data, particularly that from the Nimbus satellite, is needed. Continued monitoring and prompt data analysis are important for verifying predicted trends. Therefore, investigations that will lead to better understanding of atmospheric chemistry must continue.

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DISCUSSION

Dr. Watson: I agree that some of the measurements are somewhat disturbing; however, I think you very slightly misquote the numbers. At 38 km, that was, indeed, 2 ppb of ClO. I feel the reliability is possibly plus or minus that. The 40-km cutoff height varies ~10 percent, and not much chlorine nitrate radical ($ClONO_2$) exists at this level. At 30 km, the concentration may double. But you remember Menzies' published profile falls very, very sharply; by 30 km, it's actually well below Anderson's measurements. One must be very careful in studying a diurnal variation on the ClO-to-$ClONO_2$ process. Not much effect is seen above 35 and 40 km, but a significant effect is seen below 30 km.

Voice from Audience: In observing long-term variations in O_3, one must be aware of possible changes with the solar cycle. Although Angell's correlation of total O_3 with the solar cycle is not perfect and does not explain the whole variation, this correlation is one important factor mentioned here.

Dr. Bower: The time series analysis, conducted over a time which is longer than any cycle in question, will pick those up, and they can be factored out of the data. Hill's analysis considers this quasibiennial cycle cited by Angell, and Hill observes this approximate 11-yr cycle.

Voice from Audience: I thought you said over a 10-yr period. Right?

Dr. Bower: No. The data extend from the late 1920's in the Arosa Station. Hill examined only a recent 10-yr period for a trend. First, the entire mass of data is analyzed to evaluate what cycles may exist; then a trend is sought, in the last 5, 10, however many years, after all these established "natural cycles" are removed.

Dr. Singh: Do Jim Lovelock's data apply to perhaps FC-11 and CCl_4 and not to any of the other species we have discussed?

Dr. Bower: Only certain of the data apply to FC-11. I'm not certain they apply to the other species.

Dr. Rowland: Why do you say that if O_3 depletion is now 1.8 or 2 percent it is above the detectable limits?

Dr. Bower: Because Hill's estimate is that the detection limit is 1.56 percent.

Dr. Rowland: That is valid if it occurred at 6 yr, rather than over 25 yr. According to present models, we have not yet reached the 0.26 percent/yr.

Dr. Bower: Did Paul Crutzen not say 5 percent?

Dr. Rowland: That's his prediction for the future. I don't believe he's going to get 2 percent of the present loss.

Dr. Bower: As I remember our calculations, we do indeed find that somewhere in the vicinity of 2 percent is an expected current level.

Dr. Rowland: Yes, but that's not 0.2 percent that did not occur the last 6 yr. It is occurring over a period of 25 yr, so we are not yet at the measurable point. In one of the most recent models I've seen, we've not yet reached 0.26 percent/yr. Hill's analysis is therefore misleading, because you must reach 2 percent and then tack 1.5 percent on top of that before you start seeing a detectable trend.

Dr. Bower: I don't believe that is quite right.

Dr. Rowland: We have also carried out a least squares analysis on the Arosa data and the best fit to the Arosa data, where we factor out nothing, gives a 2 percent loss in O_3 at the end of 1977. We can't analyze the relative probabilities of 0 percent, 2 percent, and 4 percent; but it is parabolic around a 2 percent loss, and it's equally likely that we have no loss or the 4 percent.

Dr. Bower: I can't argue what you have found by a least squares analysis of the data, but that seems like a rather elementary approach to analyzing this complex set of data.

Dr. Rowland: I have a similar feeling about time series analyses of data where you know a dirty spectrometer is used.

Dr. Bower: I think we could probably argue this point until the end of the day. We are funding a lot more work by the best statisticians in the country to look at this problem. Two of them have already examined it and seem to concur that the method is valid, and we will put yet a third on it, and I think we will get the problem solved in due course.

Dr. Rowland: My statistician is currently beating the stock market at 20 percent/yr.

MEASUREMENTS OF ATMOSPHERIC METHYL CHLOROFORM BY WASHINGTON STATE UNIVERSITY

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INTRODUCTION

Several types of atmospheric measurements have been pursued by Washington State University (WSU) in the last 4 years. This research has included measurements into the lower stratosphere of various halogenated compounds, including methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF). Information on MCF vertical distribution, time trends, and latitudinal distribution has been obtained.

VERTICAL DISTRIBUTION

To obtain MCF vertical profiles, several different sampling platforms were used, beginning in 1976 with a Learjet which will reach 48000 ft (14.6 km). The first flight sequence was performed at ~47° N latitude in March 1976. Figure 8-1 shows these earliest MCF vertical profiles, which extend past the tropopause zone into the lower stratosphere. The mixing ratio data are plotted as a function of distance from the tropopause, which averaged 34500 ft (10.8 km). These data provided first proof that the models were correct — i.e., that this compound is transported at least into the lower stratosphere. At that time (March 1976) and latitude (47° N), WSU was measuring an average background tropospheric level of 95 ppt.

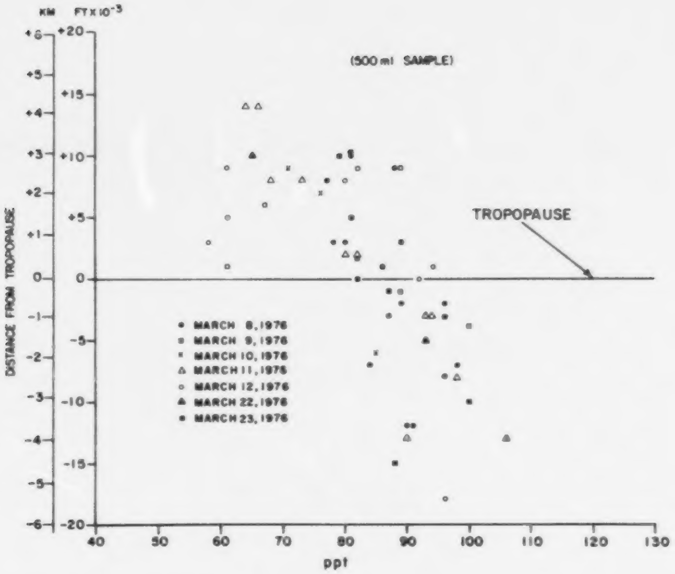

Figure 8-1. MCF mixing ratio distribution as a function of tropopause height, March 1976, 47° N latitude. From Cronn et al. 1976.

In April 1977, another set of Learjet vertical profile flights was flown off the California coast, west of San Francisco (~37° N). Figure 8-2 again shows the presence of MCF above the tropopause zone, as well as the precipitous decline in mixing ratio with ascent into the lower stratosphere. The day-to-day behavior in the low stratosphere of MCF, along with other halogenated compounds and nitrous oxide (N_2O), can often be explained by meteorological considerations (Cronn et al. 1977a,b; Saunders et al. 1978). The tropospheric level had climbed to 116 ppt by April 1977.

Subsequent measurements took place in the intertropical convergence zone (ITCZ), where the tropopause is sufficiently higher than in the mid-latitudes to justify the coupling of a U-2 with a Learjet, to extend the sampling platform to 70000 ft (21.3 km). Figure 8-3 shows the vertical distribution obtained near the Panama Canal Zone at ~9° N latitude in July 1977. The rate of decrease in the lower stratosphere was less in the tropics than in the mid-latitudes of the Northern Hemisphere (NH). This result is to be expected if the tropics are an area of upward transport of tropospheric air into the stratosphere.

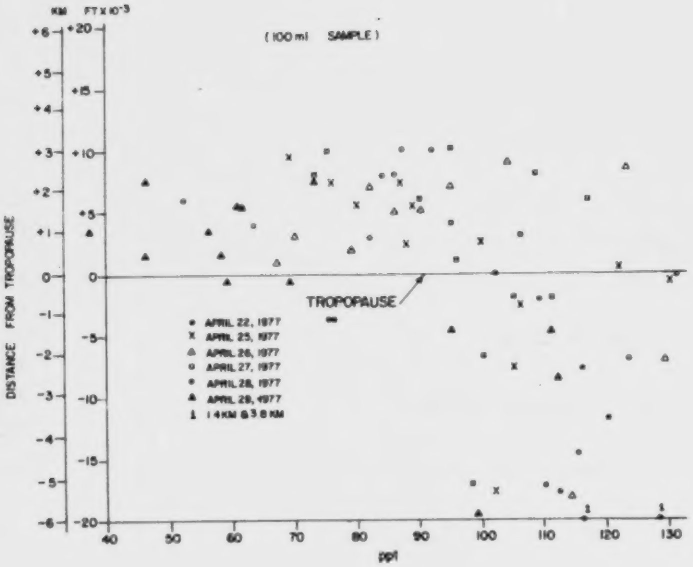

Figure 8-2. MCF mixing ratio distribution as a function of tropopause height, April 1977, 37° N latitude. From Cronn et al. 1977a.

TIME TRENDS

WSU also addressed time trend measurements of MCF. Documentation of the increase in MCF enabled accommodations with emissions data and expected sinks. Starting in July 1977, MCF data were collected at a ground station in eastern Washington State at ~47° N latitude. Figure 8-4 shows the results of that monitoring program as weekly averages of hourly measurements. The data have not been screened for incursions of high mixing ratios due to transport of air parcels with recent anthropogenic contacts. As reported earlier (Cronn et al. 1978), increases of >12 percent/yr in the MCF mixing ratio have been observed.

Figure 8-5 shows MCF measurements by various investigators in both the NH (open symbols) and Southern Hemisphere (SH) (filled symbols). This plot is similar to one reported by Neely and Plonka (1978). Data from Rowland (private communication, 1978), Singh et al. (1979), and our own laboratory (Cronn et al. 1976; Cronn et al. 1977a; Robinson 1978) were added to the Neely and Plonka data. We compared the results of our MCF modeling efforts with this data set.

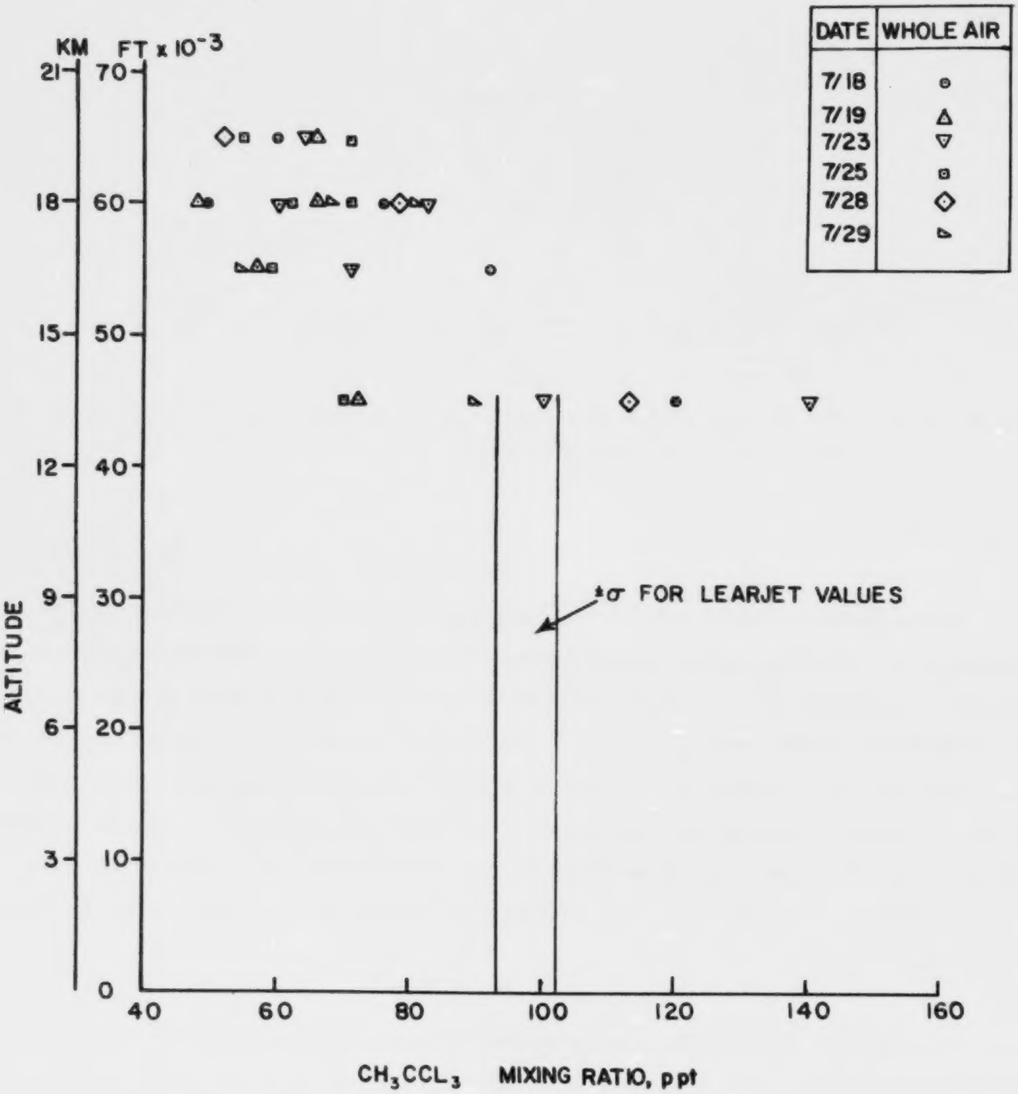

Figure 8-3. MCF mixing ratio distribution as a function of tropopause height, July 1977, 9° N latitude. From Cronn and Robinson 1978.

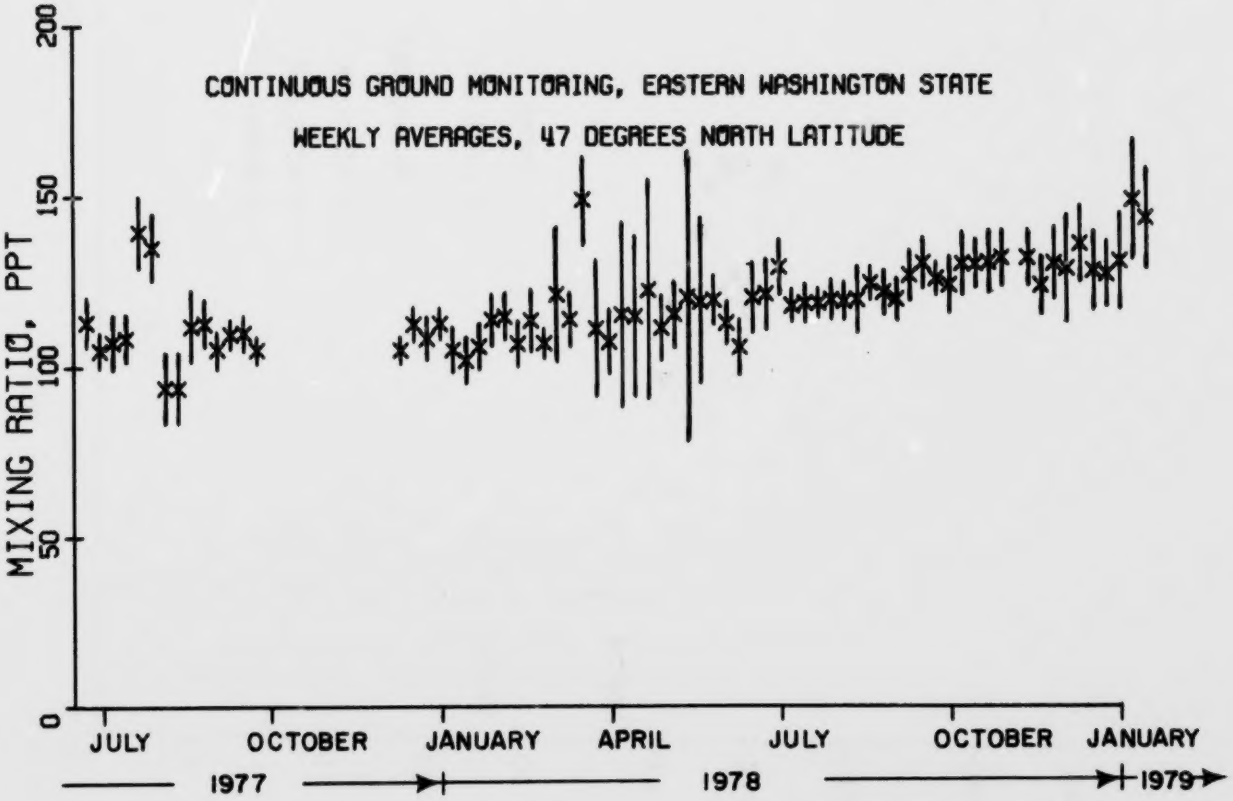

Figure 8-4. Ground-level time trend measurements for MCF, June 1977 through January 1979, 47° N latitude.

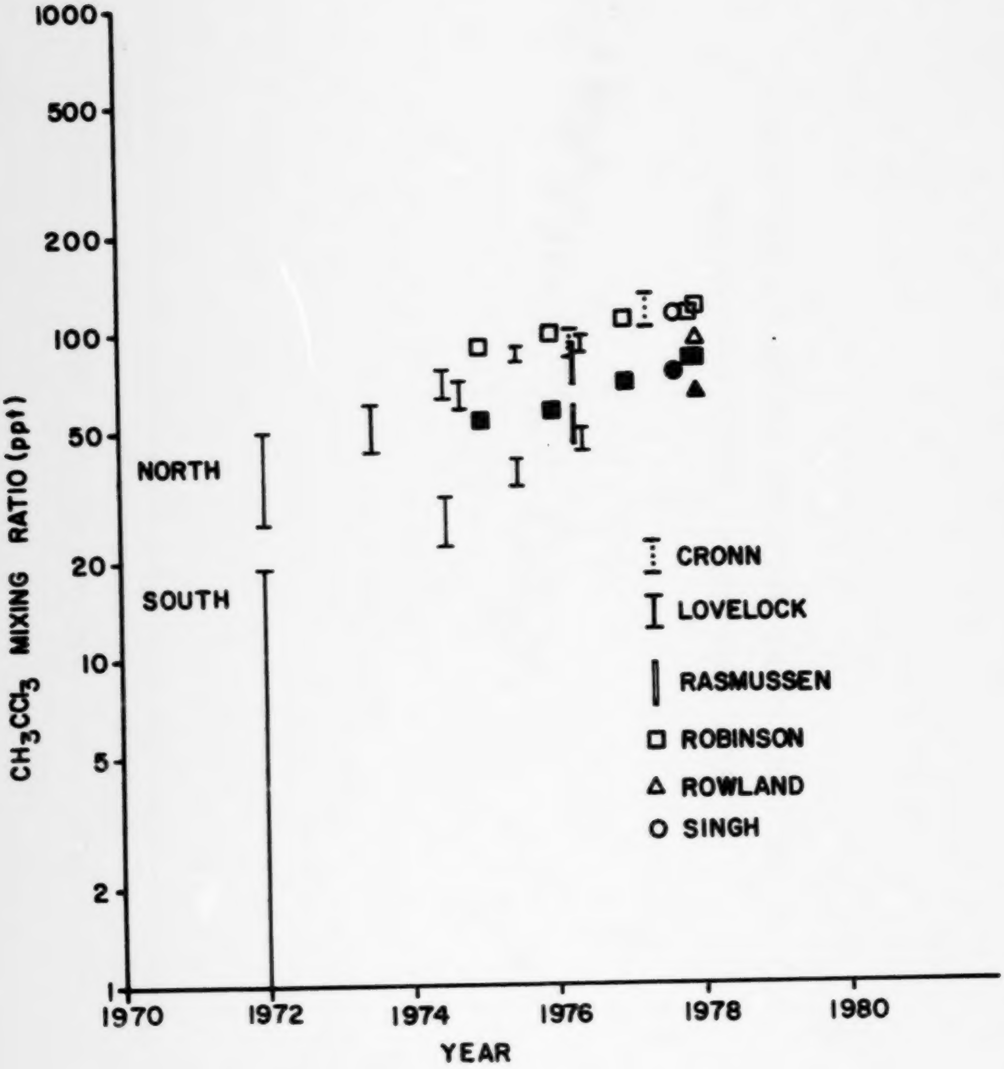

Figure 8-5. Observed NH and SH mixing ratios for MCF, 1972 through 1978.

LATITUDINAL DISTRIBUTION

The third type of atmospheric MCF measurement provided data on latitudinal distribution. Figure 8-6 shows the tropospheric MCF mixing ratio as a function of latitude for samples collected and analyzed during the second half of 1978. The data are corrected to November 1978, assuming a 1 percent/month rate of increase. Most of the data shown in Figure 8-6 were collected on board a Navy C-130 aircraft used for air chemistry measurements as part of the U.S. Antarctic Research Program. This aircraft collected data between ~35° N and ~90° S latitude. The latitudinal distribution was extended a bit further north via samples collected using the WSU Aero Commander. The latitudinal gradient seen in Figure 8-6 supports the earlier observation of a gradient obtained from comparison of the average of 97 ppt at 9° N (July 1977) with the average of 115 ppt at 37° N (April 1977). This latitudinal gradient is similar to those reported by other speakers at the Conference on Methyl Chloroform and Other Halocarbon Pollutants.

For comparison with results from other laboratories, the WSU mixing ratio for ground-level continental air at 47° N latitude in November 1978 is 131 ppt. This is the average over a 4-week period of hourly measurements from the continuous monitoring site in eastern Washington State. Urban levels can, of course, be much higher. For example, an MCF level of 1.1 ppb was measured at 2000 ft (610 m) over the Riverside, California airport in May 1976. Ground-level measurements reached 5 ppb at Claremont, California in August 1978. Often levels do not return to clean-air background values for days at a time.

CONCLUDING REMARKS

WSU has documented the distribution of atmospheric MCF as a function of time, latitude, and altitude. Tying this data base to data on emissions and the tropospheric sink due to the hydroxyl radical (OH) provides information on MCF's trospheric lifetime which, in turn, indicates the effect of MCF on stratospheric ozone (O_3) levels.

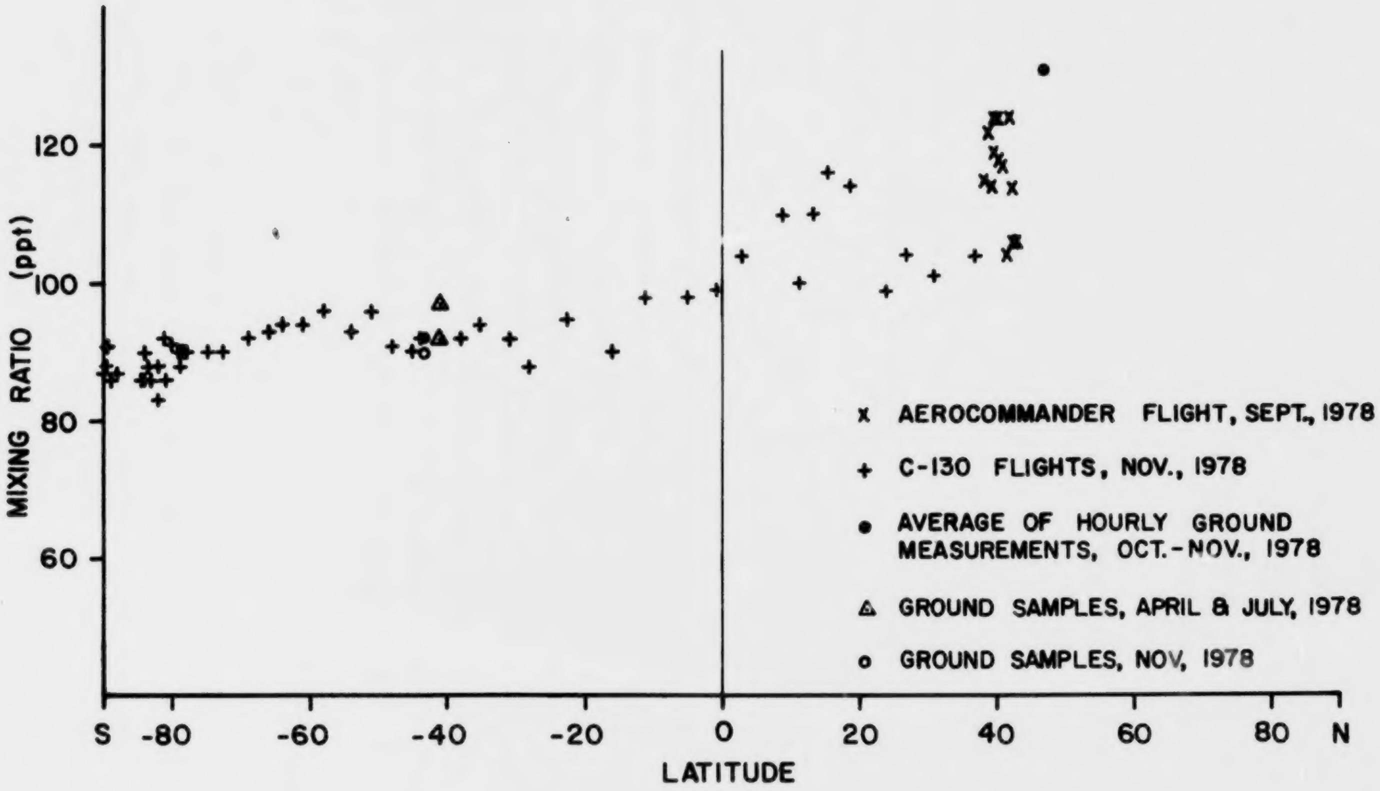

Figure 8-6. Latitudinal gradient of MCF corrected to November 1978.

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DISCUSSION

Voice from Audience: Do you have measurements of perchloroethylene (C_2Cl_4) in the SH?

Dr. Cronn: We should have some coming up, as well as analyses of the MCF data from the SH. That is not a complete data study. It contains only 50 to 75 percent of the data points, and it's not all tabulated.

Dr. Singh: Do you have any methyl chloride (CH_3Cl) data, and what do they show?

Dr. Cronn: I believe our CH_3Cl data are similar to yours; we have a larger variability in our measurements, something on the order of 5 or 10 percent standard deviation in our averages. Therefore, there is no significant statistical difference between the two hemispheres.

Dr. Hanst: You showed two graphs of MCF measurement. The second one had much more scatter in the points than the first. Why was that?

Dr. Cronn: I believe it's because of the sample size. The first graph was based on a technique that has a smaller analytical variability.

Dr. Rasmussen: To answer Dr. Singh's question on CH_3Cl, we've made fairly extensive measurements of this species as well. We have summarized the 1977 and 1978 GAMETAG flight data. Statistically, there is no difference between the hemispheres. The major differences are observed in the boundary layer in the equatorial region. The CH_3Cl was elevated in the boundary layer over the ocean. Measurements at 40°, 35°, 50° N latitude showed fewer differences. The other significant perturbations of CH_3Cl were in the slash-burned areas over East Africa. We also tried to document whether or not elevated CH_3Cl levels occurred in a forest fire in the Pacific Northwest. Apparently, the fire was too open — it was a burning fire, not a smoldering fire. The results were unequivocal. From 2 years' data (actually, now, for the third year — 1979) we don't see any interhemispheric values of CH_3Cl.

Dr. Cronn: I can comment on our data on CH_3Cl near the tropics as well. We do have published data. And in our ITCZ data the CH_3Cl was very much elevated in the boundary layer over the oceans relative to the concentrations higher up.

Dr. Rowland: What were the CH_3Cl results for the slash-burn?

Dr. Rasmussen: The values at Kenya were typically up to 3 ppb in proximity of the burn (a couple of hundred yards from very extensive burning of secondary eucalyptus fires at ~8000 ft — not Kenya proper). It was just a very wet situation where there wasn't any open fire, just a pile of smoke.

In the southern part of Kenya, we found clean air levels of around 600 to 650 ppt; levels in a smoky environment might go up to 700 ppt. In the Samburu area in the northern part of Kenya, where there's much less vegetation, CH_3Cl levels did not differ discernibly from those obtained over the Atlantic Ocean at 18000 ft.

Voice from Audience: But over Kenya, what's the fraction covered with smoke at any given time?

Dr. Rasmussen: Well, we didn't fly that close to the Ugandan border. We had enough trouble with the Somalis. But there was a tremendous pall of smoke from the western edge of Kenya all the way, practically, to Gabon on the Atlantic.

Voice from Audience: High levels were measured in the smoke itself. Does the high level fall off?

Dr. Rasmussen: Yes, it falls off. High levels of ~1 ppb or more of CH_3Cl occurred over the Indian Ocean or a tropical body of water. Elevated CH_3Cl values were also measured in the proximity of a lingering pall of smoke. Higher levels are really related to smoldering fires and not the kind of open-area fires in the Pacific Northwest where we have a rip-roaring fire going up through the open treetops. In the open flame, this buildup of CH_3Cl is not seen.

Dr. Hanst: It seems there is evidence for two sources: the oceans and the fires.

Dr. Rasmussen: We saw seen this vertical profile, Dagmar and I, on the original March 1976 flight. The samples on the flight over the Pacific Ocean were collected on a spiral from ~35000 ft on down to just off the deck. It increased progressively below the boundary layer. It was just a step function; the CH_3Cl went up. This was the first indication that CH_3Cl really was enriched in the boundary layer. And all the subsequent GAMETAG flights corroborated that — at least the samples that we have gotten.

Dr. Cronn: With a little correction: the flights you talked about were different from the ones that were plotted here.

TROPOSPHERIC HYDROXYL RADICAL CONCENTRATIONS AND METHYL CHLOROFORM REMOVAL

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INTRODUCTION

This paper describes an attempt by our group at Washington State University (Malcolm Campbell, John Sheppard, Murray McEwan, and Brian Lamb) to estimate the rate of atmospheric removal of methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF). In view of the current consensus that the MCF removal process involves oxidation by the hydroxyl radical (OH), our effort began with measured OH concentrations. In conjunction with Fishman and Crutzen's (1977) model of the variation of OH concentration with altitude and latitude, ground-level OH determinations at several sites allowed us to estimate the MCF lifetime. This process indicated a major portion of MCF oxidation to probably occur in the tropics, and at low altitudes.

METHOD

In these calculations, we tacitly assumed MCF escaping oxidation by OH to be transferred to the stratosphere. The National Aeronautics and Space Administration (1977) rate constant for the OH-MCF reaction was used. Experimentally-determined OH concentrations provided an initial basis for estimation of the prevailing concentrations; these individual OH concentrations were for a particular site and time and were not themselves global, diurnal, or seasonal averages. Many additional measurements of the OH concentration at a variety of latitudes, altitudes, and seasons will be required to permit confident estimation of the MCF lifetime.

OH measurements by our group involve the local oxidation of ^{14}CO and are described elsewhere (Campbell et al. 1979). Accuracy is believed to be about ±40%, limited mostly by wall effects. Some of our earlier data had larger error bands. The measurement is inherently an absolute measurement, needing no calibration. Our group hopes to improve the absolute accuracy of the measurement over the next few months.

For the purpose of assessing the MCF consumption rate, we selected only data that were measured in clean air representative of the uncontaminated boundary layer. These data were collected in Pullman, Washington, and at Mt. John in New Zealand. Each site is inland but not too distant from the ocean: Pullman is ~500 mi from the Pacific Ocean, and Mt. John is <100 mi from the Tasman Sea. We cannot absolutely guarantee, nor do we have measurements to prove, that the nitrogen oxides (NO_x) mixing ratios are below the 100 ppt level that distinguishes continental air chemistry and OH concentrations from marine values. However, there is no reason to expect NO_x to have been present in high concentration; certainly there are no major local sources at either site.

The New Zealand data indicated an average noontime OH concentration of $\sim 7.5 \times 10^5/cm^3$. These concentrations were measured in April and were corrected to normalize the water content. The Pullman data, measured in July, averaged $3.4 \times 10^6/cm^3$. These values were used in conjunction with the Fishman and Crutzen (1977) model in order to interpolate between 46° N and 44° S and to provide some guidance in averaging throughout the seasons of the year.

Our measured Southern Hemisphere (SH) OH concentrations were ~1/2 of what the Fishman and Crutzen model predicts. Our Northern Hemisphere (NH) figure was ~1.7 times the model prediction. Considering the experimental errors of our measurements and the inherent uncertainties of the computer-generated values, the two estimates were in essential agreement. This was rather encouraging, and suggested that the local MCF oxidation rates could be estimated within a factor of 2.

On the basis of this slender evidence, we assumed the Fishman and Crutzen model to be as good as any other for the purpose of estimating MCF oxidation rates, and we proceeded to use the concentrations generated by the Fishman and Crutzen model to estimate global MCF consumption. MCF emission data from Neely and Plonka (1978) were used along with additional data kindly supplied by Dr. Neely. A major purpose in carrying out this calculation was to examine the sensitivity of such calculations to errors in atmospheric measurements and source strength data.

RESULTS AND DISCUSSION

Figure 9-1 shows calculated contours of the rate of MCF oxidation per unit of meridional cross-sectional area as a function of altitude and latitude. This representation includes compensation for the greater surface area per degree of latitude in the equatorial regions. It is important to note that the MCF consumption contours have logarithmic intervals, and that much of the consumption takes place at low altitudes and low latitudes. These results are due to the distribution of OH concentration as a function of latitude and altitude, and to the activation energy of the MCF-OH reaction.

Figure 9-2 shows the overall rate of MCF consumption as a function of altitude. As with carbon monoxide (CO) and methane (CH_4), the consumption rate falls off rapidly with altitude. In fact, half of all consumption appears to occur below 2.4 km. This suggests that boundary-layer measurements of OH concentration are far from irrelevant in estimating the global rate of MCF oxidation.

Figure 9-3 shows the marginal distribution of the oxidation rate as a function of latitude. It is important to note how much of the oxidation takes place in the tropics; the calculation indicates half of all MCF removal to occur between 16° S and 16° N. If the model is accepted, the removal of MCF from the atmosphere becomes a "tropical affair." This domination of oxidation

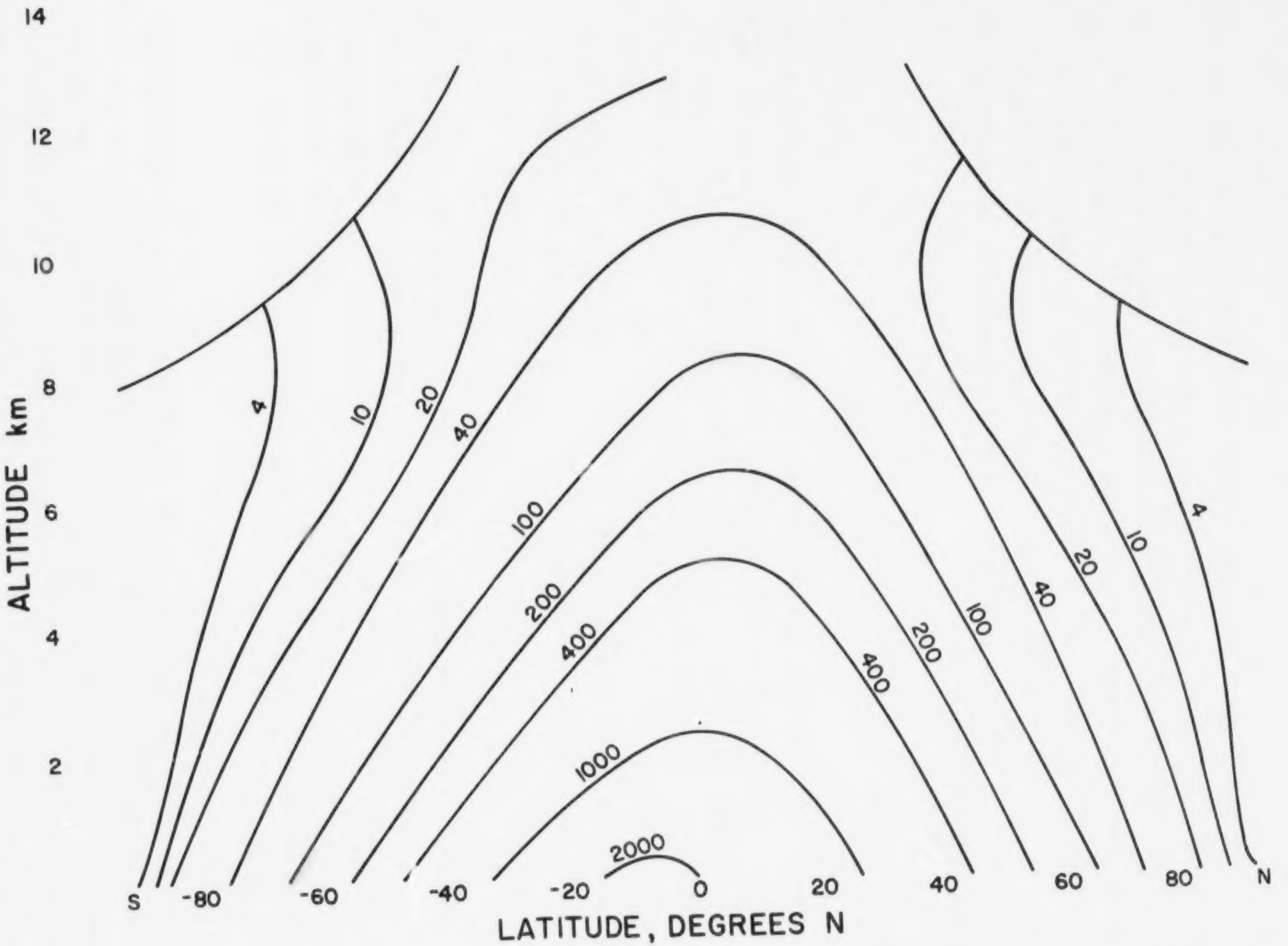

Figure 9-1. Contours of calculated MCF consumption in a meridional plane. The contour intervals are logarithmic, and the unit is 10^{12} molecules $m^{-2} s^{-1}$.

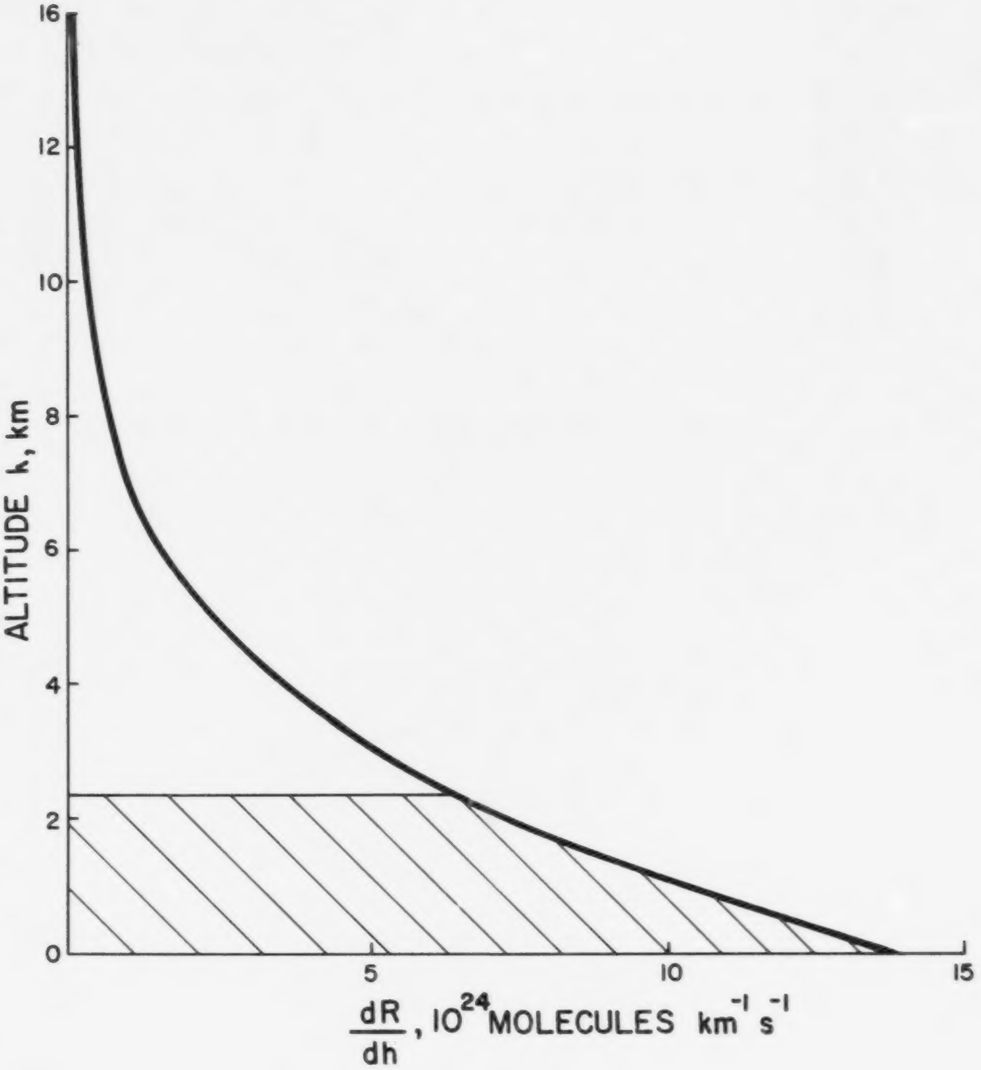

Figure 9-2. The calculated altitudinal variation of the MCF consumption rate.

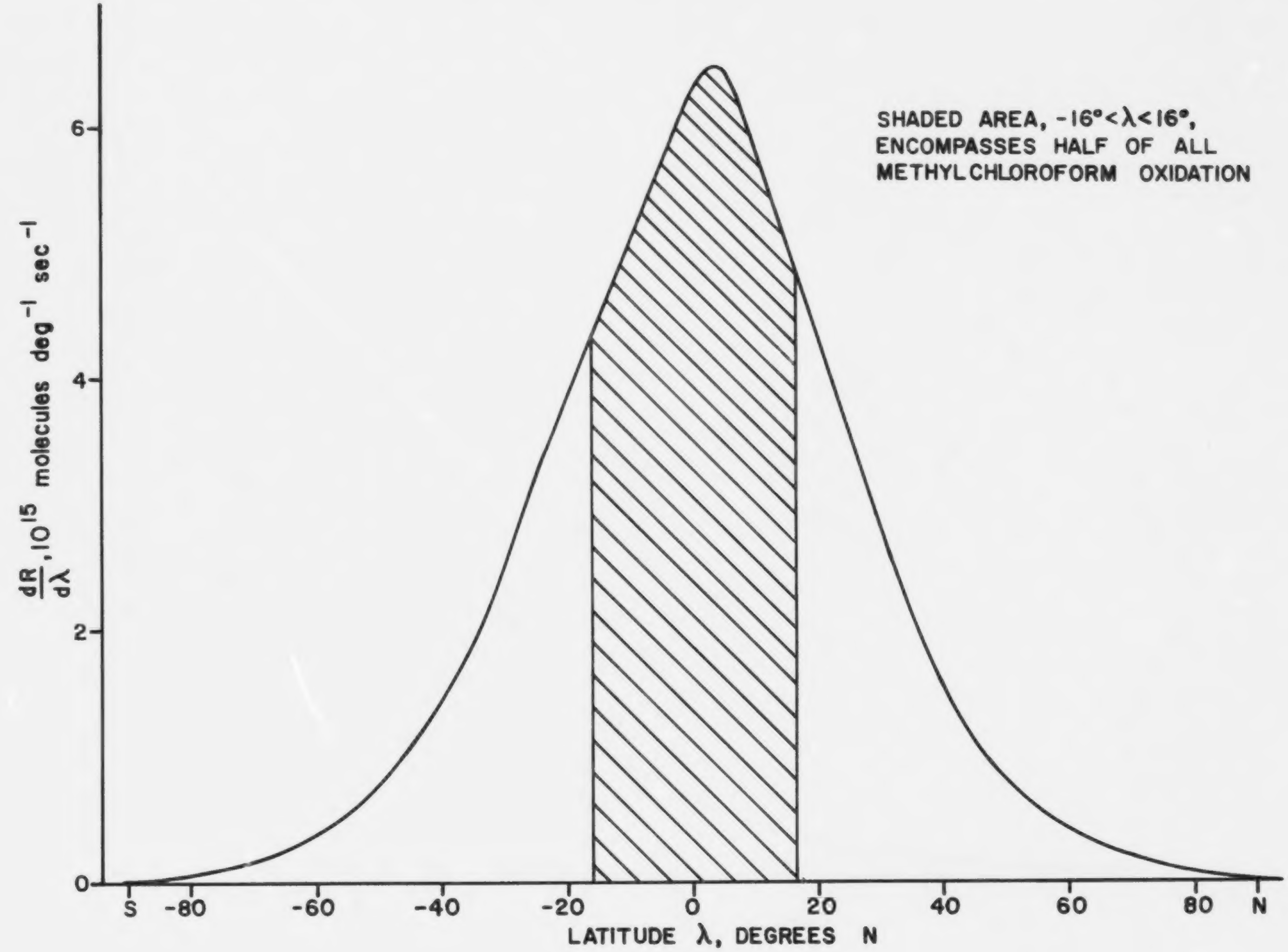

Figure 9-3. The calculated latitudinal variation of the MCF consumption rate.

in the equatorial region has an important consequence: it becomes difficult to consider the ratio of NH to SH MCF mixing ratios to reflect (in any meaningful way) the ratio of the simple hemispheric means of the OH concentrations. It is difficult, for example, to postulate a SH OH concentration that is several times the NH value when the transition from the higher SH value to the lower NH value must occur in a region within a few degrees of the equator.

From these rather crude computations, we conclude that additional tropical OH concentration data are one of the principal needs for better estimation of MCF consumption by this direct method. Our group hopes to make a number of measurements of tropical boundary-layer OH concentrations in the near future.

COMMENTS ON ALTERNATIVE METHODS

Other chapters in this volume discuss alternative methods of estimating the MCF tropospheric lifetime. These discussions do not always acknowledge that NH and SH MCF mixing ratio data, together with data on the rate of release to the troposphere, permit computation of the lifetime in two essentially distinct ways.

The first method involves comparison of the worldwide MCF burden with integrated emission data in order to determine the amount that has been lost, leading to computations of consumption rate and lifetime. For compounds with long lifetimes, this method is very sensitive to errors in either emission or absolute mixing ratio data. Essentially, the method involves calculation of a small difference between two rather large quantities. Further studies of the absolute calibration of the mixing ratio data would improve the method's accuracy.

The second method uses the ratio of the mean NH and SH mixing ratios, in conjunction with the interhemispheric transfer time. From these data it is possible to calculate the rate of consumption (or at least something close to the rate of consumption) in the SH. Data on the ratio of NH to SH mixing ratios are rather consistent, and this method would appear to be less subject to error than the first. With the assistance of Brian Lamb, our group has performed some box modeling of tropospheric MCF consumption. Reasonably good agreement with the measured NH/SH ratio is obtained, although a better fit would result from reduction of the assumed rate of consumption in the SH. The mean lifetime is 6.4 yr.

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DISCUSSION

Voice from Audience: When you say you've postulated a decrease in consumption of the SH, that's for the purposes of the model and not for your measurement?

Dr. Campbell: Yes. However, Dr. Crutzen's model and our measurements do not disagree. Our measurements are not numerous enough, at the moment, to suggest that it's wrong. Nor are they numerous enough to indicate conclusively that it's correct.

Dr. Singh: Dr. Crutzen, what do you think is the validity of your model's assumptions in the SH?

Dr. Crutzen: This was indicated in my talk [Crutzen, this volume]. In this modeling, at the moment we can get at almost any number. I don't think you can get below 10^5 molecules OH per cm^3; that is excluded. But starting from there up to 10^7 is possible. The figure depends on how much nitric oxide (NO) there is and whether you include heterogeneous factors. There are many such factors, and all we lack are the data. With MCF, there is still uncertainty as to whether or not there are some additional sources. Personally, I don't strongly believe there are, but this cannot be excluded. There are other fluorocarbons which may help the modelers get the information we're groping for.

There are unacceptably large uncertainties in the modeling effort. Also, I honestly think that we may lack some basic input in the chemistry. It's an extremely uncertain game at the moment, but that doesn't mean we shouldn't do it.

By the way, the model used by Dr. Campbell — the November 1977 model — is actually a newer model than the one I presented. Mine was the older model dating from 1975 to 1976, with the old rate constants. It was higher in OH concentrations; later, when the MCF data came in, we again adjusted our models downward to get lower numbers. Thus, Campbell's is a newer model.

Dr. Singh: Aren't we going in circles? You have a model, here, that was brought down to fit the data.

Dr. Campbell: I think that's true to some extent. Perhaps we can have a short discussion on this point: the ability of models to give information here. It seems to me that what has largely been done with the modeling to date is to use the total emission rate data and the absolute mixing ratio data to determine the OH concentration in the NH, and to then use the ratio between the NH mixing ratio data to determine the OH concentration in the SH. I believe that's equivalent to what you've done.

If that description is correct (and I believe it is), it means that the SH rates of consumption are very well estimated, but that the NH rates of consumption may be subject to considerable error. In other words, there's a question about the NH rates of consumption, but much less of a question about the SH rates of consumption. The NH rates of consumption will be pinned down only by mixing ratio measurements of greater absolute accuracy, and by more accurate estimates of the total emissions.

Dr. Bufalini: Your OH value has been so high. Have you run a model to test what side effects NO would have? As you know, Don Stedman has proposed a chemical amplifier to measure the OH and HO_2 radicals using NO.

Dr. Campbell: No, I was not aware of that proposal. On the question of sensitivity of OH to variations in NO, our model calculations suggest that it it requires nearly 0.5 ppb NO_x to make any significant change in the predicted OH concentration.

Voice from Audience: But the background levels of NO are expected to be in the low ppb, are they not?

Dr. Campbell: Not in the sites where we were making measurements.

Voice from Audience: How did you measure it?

Dr. Campbell: At Pullman, there's a record of instruments with noise levels of ~2 or 3 ppb showing no readings. The New Zealand site is, in general terms, an excellent site: a mountain range separates it from the ocean; between the mountain range and the observation site, there are probably not more than 50 habitations.

Dr. Logan: I would like to make a couple of comments. First, I think there's some confusion, here, about what is "high OH" and "low OH." Some of Dr. Crutzen's measurements and some of Dr. Campbell's measurements made at noon seem quite different.

Dr. Campbell: Roughly, by a factor of 3 or 4.

Dr. Logan: A second point I would like to make is that, from our calculation, OH values in this range are very sensitive to the amount of NO in the model. This effect is seen until NO volumes are below 10 ppt. Below 10 ppt, OH does not depend on the NO mixing ratio.

Dr. Campbell: There is another variable here, I'm afraid, where we differ. As far as the minor nitrogen species are concerned, we have not assumed that our model represents a steady state obtained over a long period of time. In other words, we've assumed that we start off, at least periodically, with relatively clean air such as is obtained after passage of a front.

Voice from Audience: My own feeling about the MCF results is that the lifetimes calculated by just taking the total assay at any given time versus total emission are the most dependable, leaving the OH out of it completely, and calculating a world average removal rate. And, as I say, it doesn't really depend very much on the mixing ratio of the mean hemisphere or how it is distributed between the two hemispheres. It's just how fast it's going away. With that, we get a lifetime of ~6 yr with almost any choice of other parameters. It's only in attempting to model north-south differences that we become involved with OH.

Dr. Campbell: It is true that the tropospheric lifetime can be estimated from production data without reference to OH. Nevertheless, the resulting lifetime estimate remains very sensitive to the absolute value of the mixing ratio.

Voice from Audience: That's right. You have to measure the absolute rate accurately and compare it with accurately known values. Then you can obtain the lifetime of MCF and use that to try to obtain the OH concentration. But you don't need to go to OH to get the MCF lifetime.

Dr. Campbell: I agree completely.

IMPACT OF BROMINATED COMPOUNDS ON THE STRATOSPHERE

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INTRODUCTION

The atmospheric chemistry of chlorinated species has been the subject of many investigations in the past few years due to removal of stratospheric ozone (O_3) by the chlorine oxides (ClO_x) catalytic chain (National Academy of Sciences 1976). Introducing brominated hydrocarbons with long residence times into the atmosphere carries potential for depletion of stratospheric O_3 similar to that by chlorinated hydrocarbons, due to a corresponding bromine oxides (BrO_x) catalytic chain:

$$Br + O_3 \rightarrow BrO + O_2$$

$$BrO + O \rightarrow Br + O_2$$

Presently the industrial production of chlorocarbon molecules is very much larger than that of bromocarbon molecules, which are considerably more expensive. Nevertheless, if future restrictions on some chlorinated compounds become severe, or if the tonnage of brominated compounds continues to increase, detailed information on stratospheric Br chemistry and its potential tropospheric bromocarbon sources will be required as a basis for regulatory action.

BROMOCARBON CHEMISTRY

The BrO_x chain is a cause for greater concern than the ClO_x chain in at least one respect (per halogen atom released) — interruption of the BrO_x chain by hydrogen bromide (HBr) formation is much less frequent than interruption of the ClO_x chain by hydrochloric acid (HCl). The abstraction reactions of atomic Br with methane (CH_4) and hydrogen gas (H_2) are both sufficiently endothermic (Hudson 1977) that neither is a factor in stratospheric reaction cycles:

$$Br + CH_4 \rightarrow HBr + CH_3$$

$$Br + H_2 \rightarrow HBr + H$$

The reaction of Br with HO_2 does occur under stratospheric conditions, as does the hydroxyl radical (OH) reaction (Hudson 1977) which returns the Br to the BrO_x cycle:

$$Br + HO_2 \rightarrow HBr + O_2$$

$$OH + HBr \rightarrow H_2O + Br$$

The absence of abstraction from CH_4 or H_2 causes Br to spend a higher fraction of its stratospheric lifetime in the BrO_x chain (chiefly as BrO, and less as HBr) than does Cl in the ClO_x chain versus HCl. However, much chemistry remains to be learned before the overall catalytic efficiency of Br for stratospheric O_3 removal can be assessed with confidence.

ULTRAVIOLET ABSORPTION SPECTRA

A key question in the overall consideration of the stratospheric Br problem now lies in the troposphere. Brominated molecules absorb at much longer wavelengths than the corresponding chlorinated molecules, with ultraviolet (UV) absorption maxima in the 200-240 nm range. The long wavelength "tails" of these absorption maxima extend into the 280-320 nm region of the stratospheric "O_3 cutoff" near 290-295 nm. Even very small absorption cross sections on the long wavelength end of 295 nm permit tropospheric photodissociation at all altitudes, resulting in greatly reduced atmospheric lifetimes and (consequently) greatly reduced stratospheric effects.

Earlier measurements of the UV absorption cross sections for brominated molecules indicated that compounds containing the $-CBr_2X$ grouping absorb sufficiently strongly beyond 295 nm to have relatively short atmospheric lifetimes. In contrast, measurements of several compounds containing the $-CBrX_2$ group (bromotrifluoromethane ($CBrF_3$), $CBrClF_2$, $CBrF_2CBrF_2$, etc.) did not indicate any absorption beyond ~280 nm (Robbins 1976; Doucet et al. 1975). Such bromofluorocarbon molecules presumably have long atmospheric residence times, and would present possibly serious stratospheric O_3 depletion problems if released to the atmosphere on a large scale.

All previous measurements employed standard short-path UV absorption cells. New measurements of the UV cross sections of several brominated molecules of industrial significance have been carried out in our laboratory in order to determine their photochemical stability, giving special attention to the very low cross sections beyond 270 nm. Several other brominated hydrocarbons have been measured as well, in order to determine general substituent effects on the photochemical cross section. The sensitivity of these measurements has been greatly increased through the use of a 2-m path quartz absorption cell attached to a Cary 219 UV-visible spectrophotometer.

In some cases the weak spectrum was measurable with a short, 10-cm cell by using sample pressures of several hundred torr. However, this approach was found to be less satisfactory because of baseline drifts, probably from sample adsorption on the cell windows. No such complications were encountered at the lower pressures used in the long-path cell experiments.

The results are summarized in Figure 10-1. Both $CBrF_3$ and methyl bromide (CH_3Br) have cross sections in the 10^{-23} cm^2/molecule range near 280 nm, and negligible absorption cross sections beyond 295 nm. The other four molecules all exhibit cross sections in the 10^{-22} cm^2/molecule range or larger near 295 nm (10^{-21} cm^2/ molecule for CBr_2F_2) and consequently may undergo

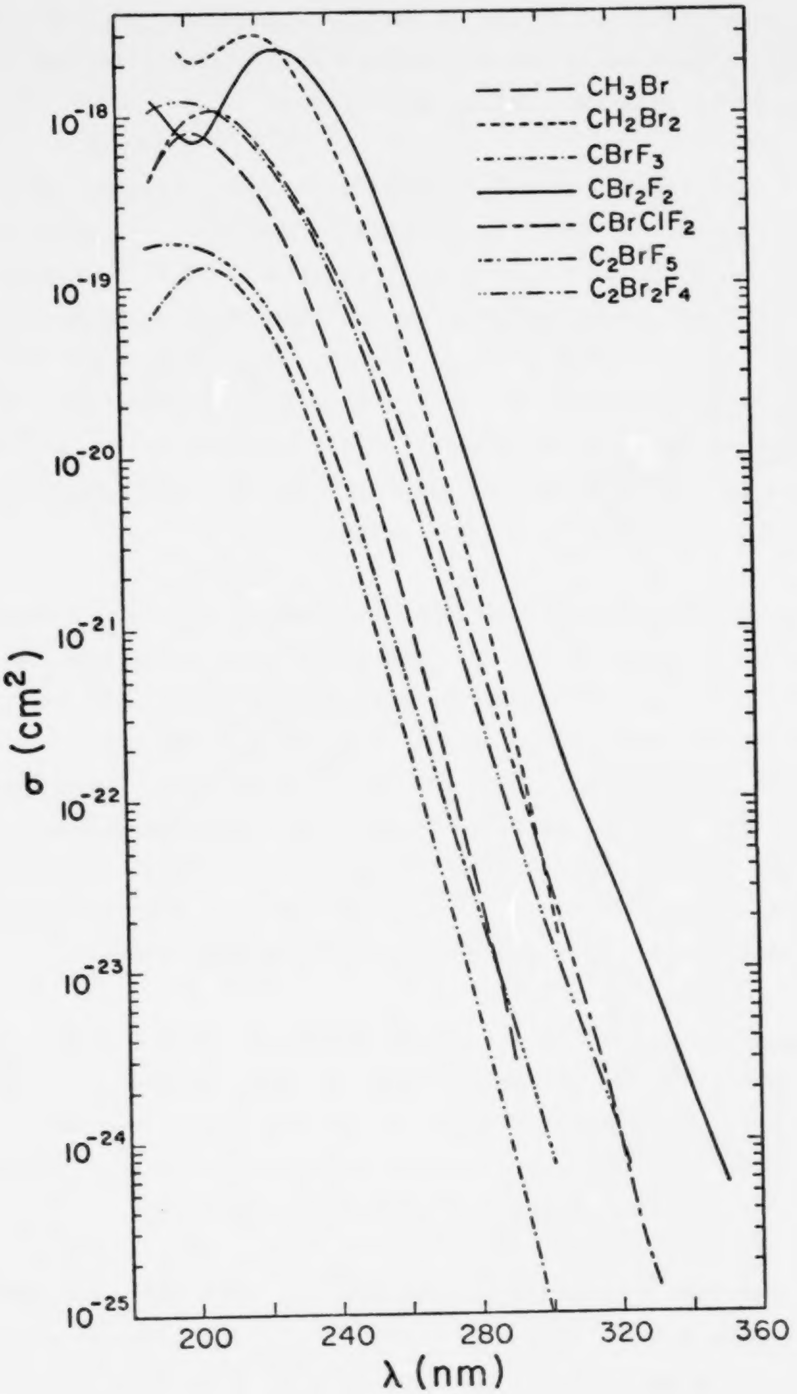

Figure 10-1. Absorption cross sections for several brominated hydrocarbons.

solar photodissociation in the troposphere. The apparent absorption cross sections for $CBrClF_2$ and $CBrF_2CBrF_2$, while very small, are sufficient to create an important tropospheric photochemical sink. However, these measurements are very sensitive in tracing impurities that might be present in the bromofluorocarbon molecules. The presence of 0.1 percent molecule impurity (such as CBr_2F_2 in $CBrClF_2$ or CBr_2FCF_3 in $CBrF_2CBrF_2$) would cause substantial perturbations in the measured cross sections beyond 295 nm. Comparison of the calculated tropospheric lifetimes of these two molecules ($CBrClF_2 > CBrF_2CBrF_2$) illustrates the importance of the "tail" between 300-320 nm for its apparent more rapid removal. The current measurements actually furnish only lower limits on the tropospheric lifetimes of $CBrClF_2$ and $CBrF_2CBrF_2$.

ATMOSPHERIC PHOTODISSOCIATION RATES

Neither CH_3Br nor $CBrF_3$ photodissociates in the troposphere (although CH_3Br is rapidly removed by reaction with tropospheric OH). Some preliminary estimates of atmospheric photodissociation rate, J, for the other three bromofluorocompounds have been carried out under the assumption that the cross sections in Figure 10-1 are accurate. For overhead sun conditions, at mid-latitudes, and at the earth's surface, the values (in units of s^{-1}) are about 6×10^{-9} for $CBrF_2CBrF_2$; 1×10^{-8} for $CBrClF_2$; and 2×10^{-7} for CBr_2F_2. The corresponding tropospheric lifetimes, using average J values that are half of those given above, are $CBrF_2CBrF_2 \geq 10$ yr; $CBrClF_2 \geq 6$ yr; and $CBr_2F_2 \geq 5$ months. The stratospheric lifetimes of the first two are ~30 yr, so that approximately ≥20 percent of $CBrClF_2$ photolysis and ≥30 percent of $CBrF_2CBrF_2$ photolysis occur in the stratosphere.

The steady-state distribution with altitude for $CBrF_3$ in the stratosphere has been calculated using a one-dimensional model and Chang's "eddy diffusion" coefficient (Hudson 1977). The atmospheric lifetime corresponding to this stratospheric dissociation process is ~50 yr. At present, $CBrF_3$ is the only brominated hydrocarbon of current technological importance for which tropospheric photodissociation is certainly unimportant.

The existence of tropospheric sinks other than gas phase solar photodissociation may have to be considered for the bromocarbons. This question has been discussed rather extensively in the case of chlorinated hydrocarbons (National Academy of Sciences 1976; Hudson 1977). Sinks such as hydrolysis in the oceans or photodissociation of adsorbed molecules may play a significant role for species such as $CBrF_2CBrF_2$, though the possibility is not likely.

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BRIDGE BETWEEN THE SCIENCE AND THE REGULATORY NEEDS

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INTRODUCTION

The U.S. Environmental Protection Agency (EPA) uses and is highly dependent on scientific information in carrying out its responsibilities. This paper discusses the kind and quality of scientific information that is valuable to policy and regulatory decision-makers.

REGULATORY CONCERNS

Methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF) and other halocarbons have been detected virtually over the entire globe; atmospheric concentrations, according to some data, are increasing significantly. Researchers who feel action should be taken to control (or not control) MCF should therefore transmit that information to regulatory policy-makers. The first questions in a series of many to be answered are: What atmospheric circumstances do these data reveal, and what should be done about them? What effects will result from increased concentrations of halocarbon contaminants in the atmosphere, aquatic systems, soils, or flora and fauna? When will these effects occur? How much of a particular pollutant exists or is created naturally? What is man's contribution to that pollutant concentration?

Even more fundamental questions are: How much of a concentration can the environment or man or other living creatures tolerate? Is there an acceptable threshold level? What are the effects of man's contributions to the pollution problem, and can preventive action be taken to reverse the situation of increasing concentrations that lead to undesirable events in the future? Over what time period will such action occur, and with what degree of control of the pollutant?

Policy- and decision-makers weigh the pertinent factors at hand to reach their regulatory decisions, and thus must have all relevant information available to them. Though absolute scientific certainty is preferable, of course, complete accuracy is not attainable in the real world. Controlled global experiments in which many variables are held constant and only one or two varied cannot be performed; the natural processes and scales of nature are in continuous flux. Even to obtain health effects data, epidemiology is virtually the sole means, since human subjects are not used in the laboratory to study carcinogenesis or other serious effects.

But responsible regulatory decision-making can be carried out in the absence of absolute certainty, because many types of uncertainty can be evaluated (e.g., through assessing data quality or determining the degree of confidence existing in the basic structure of a pollutant model). Knowing the magnitude of uncertainties associated with a data set is critical, and decision-making must be informed of error bars and the upper and lower bounds of data, the completeness or incompleteness of theory models, and any qualifying hypotheses underlying the models or analyses.

Frequently, however, data are presented as a collection of points, with or without error bars. A question pertinent to the use of such data is: If the error bar extremes (either on the high or the low side across the graph) happen to be true values, or are actually the real values with much smaller errors, would the resulting conclusions drawn from the data be the same as those postulated using the data as points? Not necessarily. Illustrations are commonly presented — even in published literature — where the measured or calculated data points in a graph are connected by a straight line or carefully shaped curve. An example is a specific case in which curves were determined by a polynomial or several polynomials whose coefficients were based on

10 or 20 percent errors, then were stated to 3 or 4 significant figures in accompanying tables; the curves were drawn very precisely without an error band width.

Again, theory credibility is important to insure that crucial factors are not overlooked, or that parameters dismissed as insignificant may not later be indeed significant. The question to be answered is: What is the sensitivity of the pollutant model, or predictions based on experimental points, to such parametric changes as different reaction rates?

Situations may occur, as with the currently pressing question of stratospheric ozone (O_3) depletion, that may not permit the luxury of waiting for absolute certainty. These situations are especially urgent if the act of delaying corrective measures causes the measures, when eventually implemented, to be ineffective for many decades. Mankind and the global environment would thus suffer greater damages for several decades or generations, as well as during the interim period before action was taken.

Such decisions — whether to regulate now or later, or whether to regulate at all — depend on knowledge at hand, and especially on the confidence in that knowledge.

A data set or model may have a 1-σ or 2-σ confidence level; these confidence levels may warrant controls of some sort. Of course, the probability that events will occur outside the $\pm$1- or $\pm$2-σ boundaries is real, but this probability is significantly lower than the probability for events to occur within the bounds. Furthermore, a decision based on an event occurring inside these 1- or 2-σ bounds may differ totally from a decision based on an event occurring, say, above or below the bounds.

A useful illustration of this situation is the fluorocarbon effect on stratospheric O_3, and ensuing effects. The decision was made to regulate and ban certain fluorocarbon usages (e.g., nonessential propellants and production of fluorocarbons for these usages) by EPA, the Food and Drug Administration (FDA), and the Consumer Product Safety Commission (CPSC). The decision was based on values, so to speak, within most of the Gaussian curve of fluorocarbon values. If the real world were in the lower range of the curve, the stratospheric effects of halocarbons could be minimal, or might even cause an increase in stratospheric O_3. But the probability of this event is very low; therefore, the decision to regulate fluorocarbons was justified. Also to be considered is a real world situation in which extremely high data values might indicate a catastrophic impact on stratospheric O_3, mandating a decision for much more stringent control. The important point is that credibility or statistical value of all data must be weighed by policy-makers, so that decisions do not rest solely on one data point or model.

INDUSTRIAL CONCERNS

Now, with regard to MCF and the other halocarbons discussed, just as with the chlorofluoromethanes (CFM's), industrial concerns hinge upon the following: If future use of compound A or B will not be permitted, what substitute compounds will be permitted? Manufacturers and users need alternative chemicals, not only to maintain their businesses, but to insure employee jobs and fulfill consumer demands.

Reactivity is an important molecular property in atmospheric chemistry. CFM has a reactivity in the troposphere of almost 0, is extremely inert, and, as far as is known, has no harmful health effects (unless breathed at extreme concentrations). Because of its inertness, CFM is a very useful substance in many industries. Because of its long persistence in the troposphere, however, CFM diffuses to the stratosphere and eventually causes an O_3 decrease.

The reactivity of other halocarbons and hydrocarbons may be high in the troposphere, forming photochemical smog and causing reactions in the troposphere that cause or contribute to poor air or water quality. These chemicals are harmful to health or ecosystems, but at least the range of atmospheric damage is confined to near ground level in the troposphere. Tropospheric lifetimes are short because reactivities are high; no significant quantities diffuse to the stratosphere.

Does a middle value or regime of values or properties exist for a whole class of substances, such as hydrocarbons, that may be established as a guide? Some chemical compounds are known to be inside or on the border of a regime. Future research may identify other characteristics rendering them uniquely acceptable or unacceptable. Such a property regime needs to be identified and established as a guide for selecting, developing, or substituting industrial substances.

CONCLUDING REMARKS

The decision-making process over the past few years has been growing more complex. EPA (along with other agencies, presumably) has always accumulated the available scientific knowledge pertinent to pollutants and resulting effects. EPA also considers the instrumentation necessary to measure substances in the laboratory and to monitor substances in the environment. Furthermore, consideration is given to control options or measures.

EPA additionally analyzes the socioeconomic impact of pollutant regulations. Costs examined include not only the price of control equipment or the economic impact of regulations, but also the cost to health, to materials, to other living things, to the quality of life, and so forth. Decision-makers consider all of these factors in creating an integrated assessment of the problem. Assessments are made available to the general public, scientists, and industry. After much deliberation and reevaluation, a final regulatory decision is made.

To return to the original point, scientific evidence is the basis for identifying and measuring environmental damage, for identifying the pollutant or other cause of the damage, and for suggesting corrective measures. Elucidating uncertainties in scientific data or models is therefore an important element in presenting factual information, creating scientific models, or proposing scenarios of probable future events. Additionally, greater understanding of gaps or differences in scientific data permits a more judicious perspective of experimental data that may be open to several interpretations within the scientific community.

DISCUSSION

Dr. Slobodow: You raised one question and I didn't hear the answer. Is there optimum reactivity?

Dr. Wiser: That is what I am asking the audience to define. Is it possible to identify an optimum reactivity or a regime of acceptable activity? We don't have an answer.

Dr. Campbell: This is perhaps an unfair question, but could you comment on how EPA feels about the way things have gone with these fluorocarbons?

Dr. Wiser: I would rather wait for the regulatory speaker later this morning who could better answer that. I think the answer would be the same.

Dr. Bufalini: I am not sure I really agree with the concept of an acceptable reactivity. According to the way EPA has gone with reactivity, it would seem that all hydrocarbons could be classified as reactive to some extent, depending on concentration. As a matter of fact, I think most modelers here agree that with sufficient methane, oxygen, and nitrogen you can, in the model, exceed air quality standards. The question then becomes: What concentration is acceptable to keep the O_3 down? It would appear that we must weigh the total concentration emitted to the atmosphere, the amount that can get into the stratosphere, as well as the amount that produces photochemical smog. I guess what I am suggesting is that if a sufficient amount of material gets into the atmosphere, it will be additive. So I think the best control is no emissions at all, obviously, but I realize that is impossible.

Dr. Wiser: I agree with your comment, except for the last conclusion. I was using "reactivity," as I said, as a catchall for the various parameters, including concentrations. There may be other characteristics that are just as important.

I disagree with your conclusion that we ought to just "stop the world." I don't think we can live with that. One of the items stated yesterday was that this year, again, auto deaths were the highest since we cut back on the speed limit. Auto accidents cause 50,000 deaths a year. We live with it. We accept it. It is a trade-off our society has made. There are many who will not accept it, and they have to live their way, but society as a whole has accepted it. So there are times when we do accept a harmful effect. Maybe it's because, individually, we believe it won't happen to us.

Dr. Singh: Just a note of caution on the reactivity. We may have species with undefined secondary products which are really more stable than the species we started with; just because the initial molecule is reactive is not sufficient grounds to go ahead and start to model it. We must consider much more than just the reactivity of the initial molecule.

Dr. Wiser: You're right. I am not going to take the time to go over it, but I just realized I omitted my discussion on sources and sinks. Thank you.

AN ASSESSMENT OF TRICHLOROETHYLENE, METHYL CHLOROFORM, AND PERCHLOROETHYLENE

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INTRODUCTION

This paper is the result of a comprehensive literature review on trichloroethylene (C_2HCl_3, TCE), methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF), and perchloroethylene (C_2Cl_4, PCE). Areas of interest include manufacturing process technology, consumption and utilization, alternatives, health impacts, ecological effects, monitoring data, and exposure levels.

After data evaluation, the need for limiting the quantities of these three compounds entering the environment was assessed. A draft of the final report has been submitted to the U.S. Environmental Protection Agency (EPA) Office of Toxic Substances (OTS), but will be modified to include data presented at the Conference on Methyl Chloroform and Other Halocarbon Pollutants.

In general, much of the information derived from manufacturing and marketing is not directly related to the theme of this paper; however, recent U.S. production quantities of the three compounds are listed in Table 12-1. All three compounds enter the environment primarily through atmospheric emissions. In the lower atmosphere (troposphere), TCE and PCE undergo photooxidation to produce the corresponding acetyl chlorides (C_2H_3ClO, etc.), phosgene (CCl_2O), and hydrogen chloride (HCl).

TABLE 12-1. RECENT U.S. PRODUCTION QUANTITIES OF TRICHLOROETHYLENE, METHYL CHLOROFORM, AND PERCHLOROETHYLENE[a]

Compound	1977	1978
TCE	298	301
MCF	635	623
PCE	614	721
Total	1547	1645

[a] Millions of pounds.

The tropospheric lifetime of TCE has been calculated to range from ~0.1 days to 6 weeks; for PCE, from 1 day to 21 weeks. These ranges of tropospheric lifetimes result from differences in methodology and rate constants used in calculations by the different research groups. Regardless, both compounds undergo relatively rapid photooxidation.

MCF, in contrast, undergoes slow tropospheric photooxidation (residence time ≈ 1 to 11 yr) to yield CCl_2O, carbon oxides (CO_x), and HCl. Because of its slow decomposition, MCF is also subject to transport into the stratosphere, where it is thought to undergo photodissociation (in much the same manner as currently hypothesized for chlorofluorocarbons) to yield Cl atoms and chlorine oxide (ClO_x) radicals. These atoms and radicals can participate in ozone (O_3) depletion reactions. Using a tropospheric lifetime of 8 yr, ~15 to 20 percent of current tropospheric MCF is calculated to reach the lower stratosphere, resulting in a steady-state O_3 depletion of ~10 to 20 percent of that calculated for the chlorofluorocarbons.

In aqueous media, the primary dissipative process is evaporation rather than hydrolysis. In one study, 90 percent evaporation was shown to occur in ~1 hour for MCF and TCE and in 1.5 hr for PCE. The ranking of these compounds in decreasing ability to hydrolyze is: MCE, PCE, TCE. TCE, in fact, is generally considered to be resistant to hydrolysis under normal conditions. The principal products from hydrolysis of MCF are acetic acid (CH_3COOH), hydrochloric acid (HCl), and vinylidene chloride ($C_2H_2Cl_2$); those of PCE are trichloroacetic acid ($C_2HCl_3O_2$) and HCl.

No data were found relating to reaction rates, decomposition products, or persistence of these compounds in soils or sediments. One study proposed that the products probably would be the same as for aqueous hydrolysis, but no confirmation was provided.

MONITORING DATA

Levels in Ambient Air

Ambient air levels at manufacturing sites were generally <2 ppb for MCF, <2.5 ppb for TCE, and <5 ppb for PCE. The highest reported average levels for any one site were 15 ppb for MCF and 14 ppb for TCE. PCE concentrations were <5 ppb at all sites.

Data for only one TCE and one MCF user site were reported. At the MCF user site, average air levels were ~4.4 ppb, or twice the average of the manufacturing sites. At the TCE facility, average levels were ~19.8 ppb, or 9 times the average of the manufacturing sites. Reported ambient air emissions from dry cleaning plants using PCE involved levels ranging from 1 ppm to >1000 ppm in outlet air vents, depending upon the sample time and the particular establishment.

Ambient air levels have been reported for 27 other U.S. cities or areas. Mean air levels for TCE ranged from undetectable to 2.92 ppb. For PCE, mean air levels reached a high of 4.5 ppb. Of the TCE sampling sites, 79 percent showed mean levels of >0.1 ppb. Seventy-seven percent of the MFC sampling sites showed mean levels of >0.1 ppb, as did 75 percent of the PCE sites.

Levels in Water

Tap water in 22 U.S. cities or areas was sampled for presence of one or more of these three compounds. TCE was detected in 14 of the cities; one city showed a level of 32 ppb, while 10 cities or areas showed levels of ≤2 ppb. The highest concentration of MCF was 17 ppb; the other 13 cities showed levels of ≤1 ppb. For PCE, the highest level was 2 ppb; the remaining 12 cities had concentrations of ≤0.4 ppb.

Nontap water concentrations were measured at 6 manufacturing sites, 1 TCE and MCF user site, 3 dry cleaning establishments, and 204 other U.S. sites. At the manufacturing sites, levels upstream from the plant outlets ranged from 0.4 to 353 ppb for TCE and from 0.1 to 132 ppb for MCF. At the plant outlets, levels ranged from 74 to 535 ppb for TCE and from 5 to 344 ppb for MCF. No levels were reported for PCE at manufacturing sites. For the only user site, upstream levels were 5 and 6 ppb TCE and MCF, respectively. Downstream of the plant outlet, levels ranged from 8 to 26 ppb for TCE and from 6 to 18 ppb for MCF.

At three dry cleaning establishments, wastewater from the carbon bed adsorption system was discarded into the sewer system. PCE levels in the wastewater ranged from ~6 to 1000 ppm, depending upon the site sampled and the time during the desorption cycle that the sample was obtained.

Of the 204 other U.S. sites sampled, 95 percent showed levels of <6 ppb for TCE, MCF, and PCE. Approximately 75 percent of all sites showed levels of these three compounds to be ≤1 ppb. The maximum levels detected for MCF and PCE were 8 ppb and 45 ppb, respectively. TCE levels were the highest of the three compounds, with a maximum concentration of 188 ppb.

Levels in Soil

Only one study was found in which levels of TCE and MCF were measured in soil. Concentrations ranged from undetectable to highs of 5.6 ppb for TCE and 3.4 ppb for MCF. In the U.S., sediment levels have been measured only at manufacturing and user sites; MCF levels ranged to a maximum of ~6 ppb. There was great variation in TCE levels, which ranged from undetectable to a maximum concentration of 300 ppb.

Levels in Lower Stratosphere

A 1976 study by Rasmussen and coworkers at Washington State University reported average MCF levels in the lower stratosphere of 79 ppt.

ENVIRONMENTAL IMPACTS

Few data are available concerning the acute or chronic toxicities to environmental species of the three subject compounds, but fish appear to be susceptible to low ppm concentrations. The lowest reported LC_{50} values were 5 ppm for PCE, 16 ppm for TCE, and 33 ppm for MCF. In general, fish appear to be capable of bioconcentrating these solvents to levels of ~100 times the aqueous concentration.

HEALTH IMPACTS

The lowest chronic exposure level at which some type of human physiological effect can be consistently observed for any of these three compounds is ~50 ppm TCE. When this level of exposure is maintained for extended periods (e.g., in a work area), a large proportion of exposed individuals experience dizziness, headaches, and incoordination; these effects are reversible after the individual is removed from the exposure area. With MCF, the dizziness, headaches, and incoordination do not usually occur until levels reach ~250 ppm for similar exposure times. The effects of PCE, however, are somewhat different from those of TCE or MCF. Only ~6 percent of inhaled MCF is retained by the body — the remainder is exhaled immediately, and even the retained MCF apparently is later expired largely unmetabolized. TCE is more readily absorbed (~90 percent) during inhalation but very slowly metabolized by the body; the effects of TCE are much more prolonged than those of the other two compounds.

An epidemiological study in which workers were exposed to ~150 ppm MCF for periods of 1 to 6 yr showed no adverse health effects. There is no evidence of worker death as a result of long-term occupational exposure to MCF or the other compounds. Case histories show, of course, that deaths have occurred as a result of occupational exposure, but these cases involved accidental exposure to very high levels (~7000 ppm or more). At such levels, the very swift narcotic or anesthetic effects of these compounds render the victim unconscious, causing death from overexposure.

All three compounds (but especially MCF) can sensitize the heart to the effects of epinephrine. The required dose and exposure level, the mechanism, and the number of persons at risk from this type of sensitization are unknown. Sensitization with fatal results has been most frequently reported after exposure to high levels (~7000 ppm) of MCF.

Studies by the National Cancer Institute indicated TCE and PCE to be potential carcinogens; investigators found oral doses of the compounds to produce liver tumors in mice but not rats. Tests conducted with MCF produced no tumors, but high dosages resulted in animal data that were not suitable for statistical analysis, and no conclusions could be drawn regarding the carcinogenicity of this compound. The average daily oral doses of TCE and PCE were ~500 and ~1000 mg/kg, respectively. The results of the bioassays have created considerable controversy because of the high dose levels used, the method of dosage, and the production of liver tumors in mice only. The predominant human exposure route for these two compounds is generally inhalation, not oral ingestion, which can vitally affect distribution. The carcinogen bioassays are being repeated with improved experimental design for all three compounds.

EXPOSURE LEVELS

TCE, MCF, and PCE can be assimilated by inhalation, ingestion (food and water), and dermal absorption. The present discussion is limited to inhalation and water ingestion; no data are currently available for the presence of these compounds in U.S. food products, but this route of intake is tentatively assumed to be negligible. Quantities introduced into the body by dermal absorption are also considered negligible in comparison to inhalation and water ingestion.

Bodily levels due to inhalation were calculated for every city or area having monitoring data. For TCE, only five cities showed levels of human exposure of >1.5 micrograms per kilogram body weight per day (μg/kg/day). The highest level of those five was ~26; other levels were ~18, ~3, and ~2 μg/kg/day. Calculated exposure levels for all large cities with high population densities were ≤1 μg/kg/day. For MCF, citizens of only one city showed a calculated level of >2 μg/kg/day; data for large cities ranged from a high of 1.3 to a low of 0.1 μg/kg/day. Six cities had calculated PCE human inhalation levels of >1.2 μg/kg/day. The two data sites with the highest calculated levels were New York (7.8 μg/kg/day), and a small city. Los Angeles showed a level slightly greater than 2 μg/kg/day. In general, the available data show that a relatively small segment of the general population is exposed to TCE or MCF air levels resulting in bodily retention of >1.5 μg/kg/day, yet the same statement is not necessarily true of PCE.

Data on TCE in drinking water indicated only two cities in which citizens had calculated exposure levels of >1 μg/kg/day; the highest level was 1.6. One other city had a level of 0.95, and all other cities had levels of <0.25 μg/kg/day. Data for MCF were difficult to assess due to a lack of quantitative values. For only one city was the calculated level appreciably above 0.05 μg/kg/day. In general, large metropolitan areas showed little if any MCF in drinking water. For PCE in drinking water, only one city showed a calculated human exposure level of >0.02 μg/kg/day.

Exposure levels calculated from both ambient air and drinking water concentrations were available for few cities. One of five cities showed a total calculated human TCE exposure level of >4 μg/kg/day. For MCF, one of five cities showed a calculated level of >2 μg/kg/day. All other cities had levels of <1.2 μg/kg/day. Data for PCE were confined to two cities, both of which are metropolitan areas with populations in excess of 1 million. The highest level was ~7.8 μg/kg/day; the other level was ~1.2 μg/kg/day.

Based on the information derived from this study, including that of Mazaleski (this volume), available control options to reduce emissions of these compounds have been noted for consideration by appropriate governmental agencies. These options should not be construed as EPA policy. After consideration of all data available from all sources, EPA must determine which regulatory options, if any, should be exercised.

Generally, the data show that no basis now exists for a total regulation or cessation in manufacture of these three compounds. This statement is not a judgment that manufacture or use of the compounds pose no human or environmental risk, but rather that the data are inconclusive, at this time, with respect to such manufacturing restraints. Certain options in selected areas do appear appropriate, however, for limiting human and environmental exposure.

RECOMMENDATIONS FOR EMISSION REDUCTION AND CONTROL

In view of recent studies of MCF effects on O_3 depletion, test results indicating possible MCF-induced mutagenicity, and the report on MCF by EPA's Carcinogen Assessment Group, Midwest Research Institute (MRI) suggests that MCF does not belong in a classification of chemicals for which "it is not necessary that they be inventoried or controlled." TCE, MCF, and PCE should be considered a group and, as such, should all be subject to the same emission controls. Recently, EPA's Office of Air Quality Planning and Standards recommended that State Implementation Plans consider positive emission reduction for all three compounds, rather than substitution of MCF for either of the other two solvents. MRI believes use of emission control technologies for all three compounds to be the proper approach.

Metal Cleaning Industry

Current control technology can decrease ambient air emissions by 50 to 60 percent. A large portion of the control technologies recommended by EPA for New Source Performance Standards do not require the purchase or use of expensive equipment. Significant emission reductions can be attained by employing careful operating practices and good maintenance procedures.

A comprehensive training program must also be employed. This training program is very significant not only for vapor degreasing operations but also for cold cleaning procedures, since many cold cleaning operations are conducted by untrained and nonsupervised workers in small companies; such situations can often lead to increased human exposure and high emission losses.

Dry Cleaning Industry

MRI offers recommendations for the dry cleaning industry in view of suggested new EPA guidelines for control of volatile organic emissions from PCE systems.

Solvent Recovery and Waste Disposal

Solvent recovery techniques are currently available which, if more fully adopted, could lead to appreciable recycling of solvent and an overall reduction in the quantity of unrecyclable waste. This method should be emphasized as an initial technique to reduce quantities introduced into the environment. For the quantity of distillation residue that still remains after reclamation, the preferred means of disposal is incineration. Levels of toxic or corrosive decomposition products from incineration should be maintained at an environmentally acceptable minimum.

Contract reclamation and incineration services are generally available in the larger metropolitan areas, so many companies will be able to readily reclaim or discard their waste solvent. However, companies generating small volumes of waste solvent may find no reclamation or disposal service interested in small volumes. Additionally, large geographical areas may be without service altogether. In order to alleviate these potential problems, an appropriate federal agency could assist users (perhaps through the use of regional offices) in finding the nearest contract reclamation or incineration services.

Water Quality

Amendments and proposed amendments for control of these three compounds in water have been published. Currently, controversy surrounds a number of these statutes, and new regulations are being proposed.

With respect to concentrations in finished drinking water, methods for control of chemical contaminants have been proposed by the EPA Office of Water Supply. These proposed regulations have been debated by the water supply industry, and EPA is preparing detailed responses to resolve the issues raised during the comment period. In view of this activity, no options are suggested to modify the proposed regulations.

TCE was classified as a Category C Hazardous Substance in the EPA Hazardous Substance Spill Program, based on aquatic toxicity (96-hr LC_{50}) levels in the 10- to 100-mg/liter range; neither MCF nor PCE was identified as a hazardous substance. But the Spill Program was halted by an industry lawsuit, and revised Section 311 rules are now ready for final internal review. If, as indicated, the new Section 311 rules include only EPA's previous list of 299 substances, TCE will remain the only one of the three compounds designated as a Hazardous Substance. Since MCF and PCE exhibit basically the same type of aquatic behavior and aquatic toxicity levels as TCE, MRI feels that these two compounds should be evaluated for inclusion in the same category.

Container Labels

All three of the subject compounds appear to pose a human health problem in high vapor concentration. To explicate the potential danger, MRI suggests adequate labeling of all TCE, MCF, and PCE containers. The label should state that a high vapor concentration can cause unconsciousness or death, and that exposure to high vapor concentrations followed by strenuous physical activity or high levels of excitement or stress may result in heart sensitization. Industrial workers with previous histories of heart problems would particularly benefit from such labeling, as they may unexpectedly encounter high concentrations of the compounds.

Dental and Medical Procedures

On the basis of health effects data derived in this study, the essentiality of TCE use in dental and medical procedures must be considered more closely by appropriate agencies. Although very minor amounts are used in such procedures, TCE is introduced directly into the human body at levels considerably above those to which the general public would normally be exposed. Alternative materials can and are now being utilized in varying degrees in both dental and medical applications.

Aerosol Products

MRI suggests that use of MCF or PCE in aerosol products be considered by the appropriate agencies. As with dentistry and medicine, this area of use is minor but also represents a mechanism for potential direct inhalation. Use of aerosol products containing either of the two compounds could expose the user to high concentrations, causing a decrease in manual dexterity, eye irritation, and central nervous system effects (primarily dizziness).

The Consumer Product Safety Commission has recently announced an analysis of PCE to evaluate alternatives for regulating the chemical as a hazardous component of consumer products. A briefing is scheduled for March 1979.

DISCUSSION

Dr. Farber: I would like to make a brief comment before we lose any of the people that have heard this report to the outside world. I thought this meeting was to address the O_3 depletion issue, but I didn't hear much of that discussed in the MRI report. I understand the rest of the morning's presentations may not spend much time on that issue either. I am obviously very concerned, because about a month ago I wrote to Dr. Hanst indicating that if the subjects were to stray very far from this issue, we would like to have the opportunity to discuss these other issues in some detail with the experts that did the work. I was assured by Dr. Hanst in a return letter that the subject would be confined to these issues to the best of his ability. I think your ability is suffering, Sir, at this moment, and I am very, very upset, as you probably can tell.

Let's put it this way. If I were the manager of a baseball team, I would be playing this game "under protest." I guess that position will probably have about as much impact on what is going to happen here for the rest of the day as it does in a game played under protest! I do offer, by the way, the services of the Dow Toxicology Department and the other independent researchers whom we finance to discuss some of these areas of concern with whoever here would like to have them objectively discussed.

Dr. Hanst: While further discussion on the toxicology and health effects of these compounds may ensue, I am sure you will have the opportunity to discuss these issues at other meetings. We have confined ourselves mainly to the atmospheric chemistry, but the MRI study, made public for the first time, provides us with a rather complete picture.

Dr. Heicklen: I would like to ask a series of short questions. I gather from what you said that there are no known human effects at levels of <50 ppm.

Dr. Lapp: There are none other than any mutagenic or carcinogenic effects.

Dr. Heicklen: The human exposure levels of all three of the compounds are $\lesssim$1.5 ppb?

Dr. Lapp: Correct.

Dr. Heicklen: Can you tell me how much this control program is going to cost?

Dr. Lapp: As it stands right now, it is very difficult to try to evaluate how much it is going to cost a company to educate their people. Now, if you want to make some random —

Dr. Heicklen: You are recommending to EPA that controls be placed on this compound, with this information, without having any idea of what this program is going to cost.

Dr. Lapp: First of all, we are not involved in any cost study to begin with.

Dr. Heicklen: I don't think you should have accepted the task, then.

Dr. Lapp: Well that, unfortunately, is not your choice or mine. However, the controls recommended by EPA for degreasers and for clothes cleaners will obtain levels of roughly 50 percent if used properly, and these controls can be effected with equipment already on the degreasers. It basically is a housekeeping procedure. What the cost of that would be I don't know. I could guess at it.

Dr. Heicklen: Thank you.

Mr. Surprenant: I would like to inquire of the data base for your comment on carcinogenicity or mutagenicity, particularly for MCF.

Dr. Lapp: As you well know, as a toxicologist, I don't get involved in the health effects.

Mr. Surprenant: But you certainly did this morning.

Dr. Lapp: I know. Much of that refers to what Dr. Mazaleski will talk about. The mutagenicity effects were in the report, and I would have to look that information up for you, to be honest about it. The report showed that TCE and MCF were used.

Mr. Surprenant: Would you say that they are in any way comparable by levels of ppb or μg? What was your per-kilogram? Are they in any way in an environmental comparison to the measure of value?

Dr. Lapp: If I recall correctly, they are.

Dr. Heicklen: You say now that the Ames Test has shown mutagenicity and that the compound is therefore mutagenic; but the Ames Test is a screening test.

Dr. Lapp: That is right, and it is one of eight sets.

Dr. Heicklen: I am familiar with some of these toxicological tests, and this test targets a compound for further investigation. Although mutagenic activity was observed in bacteria, those test results do not necessarily apply to humans. It is a compound that should be further investigated because, in fact, some researchers do suspect a problem. But to extrapolate from the Ames Test that this compound is going to be mutagenic in humans is unwarranted. Such a conclusion is not warranted from Ames Test data.

Dr. Lapp: We did not say that it was "mutagenic." We said it was "potentially mutagenic."

Dr. Fisher: It is not a ridiculous extrapolation at all.

Dr. Heicklen: I didn't say it was a "ridiculous extrapolation."

Dr. Fisher: The Ames Test, as a test for mutagenesis, is quite good. For carcinogenicity, its value is only as a screen.

Dr. Heicklen: For mutagenicity, there are false positives and false negatives. It is a good screening test, or you wouldn't use it, but it is still a screening test.

Dr. Fisher: For a direct test in mutagenesis.

Dr. Heicklen: In bacteria.

Dr. Bower: Let me get back to the topic of the conference. Now, you quoted U.S. production figures for these various materials. From the standpoint of modelers who want to model stratospheric effects of materials, estimates of worldwide production (with estimates of errors) are generally much more useful than U.S. production figures. Yesterday, Dow quoted figures on MCF excluding Soviet production. Now, I am sure that Dow can arrive at a much better estimate of Soviet production than can the average modeler. From that standpoint, then, I think it would be very useful to have an estimate of worldwide production.

METHYL CHLOROFORM AND ITS STABILIZERS

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INTRODUCTION

The main topic of this paper is the ongoing U.S. Environmental Protection Agency (EPA) investigation into health effects of methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF) and a number of MCF stabilizers, particularly the dioxane/MCF and dioxolane/MCF mixtures of The Dow Chemical Company and PPG Chemical Industries, respectively. The viewpoints presented herein are the author's scientific opinion, not the official position of EPA. Specific EPA policy has not yet been finalized, because EPA's Office of Toxic Substances is currently reviewing very recent and pertinent data on MCF. Any official EPA statements could have significant impact on the chemical, which is extremely high volume and in common use worldwide.

In December 1978, the author prepared an extensive 103-page report on MCF and MCF stabilizers as Section 4(f) of the Toxic Substances Control Act (TSCA) Support Document for 1,1,1-Trichloroethane (Methyl Chloroform) (Mazaleski 1978). The report contained 88 references, including a citation of the Dow study on MCF inhalation in rats. This very critical Dow study appears deficient in protocol and methodology. A preliminary assessment of the Dow study issued on January 17, 1979 by EPA's Carcinogen Assessment Group for MCF (U.S. Environmental Protection Agency 1979) is summarized below. Also outlined are deficiencies in the studies of PPG Chemical Industries on dioxolane as an MCF stabilizer. Stabilizers are a source of concern; in January 1978 dioxane itself was shown by the National Cancer Institute (NCI) to be carcinogenic in two animal species under test conditions. This research supports work performed several years earlier by Argus et al. (1973). Difficulty was encountered with the criteria document on dioxane by the National Institute of Occupational Safety and Health (NIOSH); although published in September 1977, the NIOSH report did not include a major metabolite, p-dioxane-2-one, which is reported to be 8 times more toxic than dioxane (itself a moderate carcinogen).

BACKGROUND AND OVERVIEW

MCF is used primarily as a cleaning or degreasing agent for metals. It is increasingly used as a substitute for chlorinated ethylenes, such as trichloroethylene (C_2HCl_3, TCE), which is carcinogenic. An estimated 630 million pounds of MCF were produced in the U.S. in 1976. At least 300 million pounds were dispersive uses, primarily for metal degreasing and for aerosols. MCF escapes into the environment primarily into the air, and may affect the ozone (O_3) layer in the upper atmosphere. NIOSH judges that 3 million workers may be exposed.

Methylene chloride (dichloromethane, CH_2Cl_2) is soluble in water, TCE is less soluble, and MCF is insoluble. The boiling points of the three compounds are: 40° C (CH_2Cl_2), 74° C (MCF), and 87° C (TCE). The most harmful effects of MCF involve central nervous system problems, including anesthesia, disturbed equilibrium, and impairment in perceptual speed and dexterity. MCF cardiovascular effects include decreased blood pressure, bradycardia, and hypertension. Exposure can also cause inflammatory changes in the lung, fatty changes in the liver, and damage to the kidney. MCF is eliminated from the body in unaltered form via the lung.

Dioxane and MCF may have an effect on birth anomolies. The Dow Chemical Company sent data on impurities to EPA in late December 1978, and (under the Freedom of Information Act) requested from EPA's Carcinogen Assessment Group a document entitled "Dioxane: A Critique." This particular report (Mazaleski and Schumacher 1978) indicates that birth defects may occur from MCF/dioxane or from MCF itself. There is some concern that MCF, under conditions of storage or usage, may degrade to vinylidene chloride ($C_2H_2Cl_2$), a suspected carcinogen. Louis Schlossberg of Detrex Chemical Industries has suggested that these conditions are presence of water, iron, zinc, aluminum, or chloride salts of these metals. Thus, gray areas concerning hazards of MCF do exist.

In April 1978, the Interagency Testing Committee placed MCF on its priority list for testing. EPA has been working closely with The Dow Chemical Company and Detrex Chemical Industries to produce a document on possible regulation of MCF; the following data are taken from Mazaleski (1978).

MCF was introduced to industry with an improved inhibitor system that provides better corrosion protection and stability under vapor degreasing conditions, and enables it to compete with TCE in vapor degreasing applications. Stabilizing grades of MCF are made by the addition of 3 to 8 percent stabilizer composed of various chemical constituents, which are reported to include nitromethane and N-methylpyrol, 1,4-dioxane, butylene oxide, 1,3-dioxolane, and secondary butyl alcohol. Commercial products are reported to contain amounts of certain stabilizing materials, including p-dioxane (a stabilizer MCF additive sold by Dow). In 1978, NCI reported dioxane to be quite carcinogenic in test animals. Dioxolane, a stabilizer MCF additive utilized by PPG Chemical Industries, is currently being tested to determine if it is also carcinogenic (Mazaleski 1978; Bell 1978).

According to oncogenicity information obtained by the EPA Carcinogen Assessment Group in January 1979, MCF is a suggested carcinogen. However, the Group categorizes different levels of carcinogenicity, and no data sufficient to calculate a human risk assessment exist. In-vitro tests (the Ames test and a cell transformation test) suggest that MCF is less potent than CH_2Cl_2 and similar in potency to TCE (U.S. Environmental Protection Agency 1979).

No studies adequately assess the carcinogenic potential of MCF. A lifetime animal bioassay at the maximum tolerated dose (MTD) is required to characterize carcinogenic potential; such a gavage study is in progress at NCI for rats and mice. An earlier NCI study (National Cancer Institute 1977) was inconclusive, due to poor survival of treated animals. An inhalation study in rats by Dow (Quast et al. 1978) showed no evidence of carcinogenicity, but the doses were given for only half of the animal's lifetime, and the highest dose did not appear to be an MTD. Comparison of doses in the Dow study and the early NCI study shows that the MCF toxic dose by gavage is less than the toxic dose by inhalation.

With regard to a Manufacturing Chemists Association TCE inhalation study in rats and mice (Bell 1978; Van Horn 1978, 1979), the precision of controls seems open to serious question. In fact, the data from this $500,000 study appear unusable, disallowing valid conclusions linking carcinogenicity with TCE.

IN-VITRO STUDIES

In application of the Ames Test to these compounds, it is necessary that bacteria be exposed to the compound of interest in a desiccator or in liquid suspension. If this precaution is not taken, false negatives may result.

MCF was weakly mutagenic in strain TA100 when the Ames Test was conducted in desiccators (Simmon et al. 1977). A measured volume of MCF was placed in an open dish in the bottom of a desiccator, and the open petri dishes containing Salmonella strains were placed in the top of the desiccator. Exposure occurred for a set number of hours. MCF was less potent than CH_2Cl_2 and about equal in potency to TCE, and was mutagenic in the presence and absence of metabolic activation using Arochlor 1254-induced rat liver. A dose response was evident, but the number of revertant colonies was only twice control plates at the highest dose tested: 750 μl in an open dish in a 9-liter desiccator.

MCF was also tested by Litton Bionetics for Dow, but the methods and data were not available for evaluation. In other data from Dow, however, MCF with metabolic activation gave a positive response in strain TA1535, an equivalent response in TA1537, and a negative response in TA1538 (Farber, personal communication). Strain TA100, which is a more sensitive derivative of TA1535, was not tested. These results are consistent with the more careful study by

Simmon et al. (1977). Henschler et al. (1977) reported that MCF was negative in TA100, but these authors used no precaution to insure that the bacteria were actually exposed to the highly volatile compound.

MCF altered cells in an in-vitro test of cell transformation performed using Fischer rat embryo cell line F170 (Price et al. 1978). When injected, these cells produced fibrosarcomas in 8 out of 8 rats. In this test, MCF was less potent than CH_2Cl_2 and similar in potency to TCE.

IN-VIVO STUDIES

National Cancer Institute Study

The 1977 NCI carcinogenesis study in rats was inconclusive due to poor survival of treated animals, and the NCI Clearing House of Environmental Carcinogens resolved that carcinogenicity cannot be determined at the present time (National Cancer Institute 1977). In this 1977 study, Osborne-Mendel rats were treated by gavage with both 750 mg/kg and 1500 mg/kg of MCF in corn oil 5 times/week for 78 weeks. The rats were observed an additional 32 weeks, with the experiment ending at 110 weeks. Both males and females were used, with 50 of each sex at each dose and 20 untreated females. The study was inadequate because only 3 percent of treated rats survived the length of the experiment. There appeared to be an anticarcinogenic effect on fibroidadenoma of the breast.

The 1977 NCI bioassay also employed $B6C3F_1$ hybrid mice. The study used 20 mice of each sex in the control group and 50 of each sex at each treatment dose. The time-weighted average dose was 2807 mg/kg and 5615 mg/kg. The mice were treated by gavage 5 days/week for 78 weeks and observed for another 12 weeks, for a total of 90 weeks in the experiment. Only 31 percent of treated animals survived to the end of the experiment, and treated animals gained less weight than controls. In male mice, an excess of tumors seemed to occur in the liver (1 tumor among control animals and 7 tumors among treated animals), but this increase was not statistically significant.

As mentioned previously, a 2-yr carcinogenesis bioassay by gavage in mice and rats is underway at NCI.

Dow Chemical Company Study

The Dow study (Quast et al. 1978) treated groups of Sprague-Dawley rats by inhalation under conditions similar to those experienced by workers (6 hours/day, 5 days/week, for >1/2 lifetime). The rats were treated 12 months and observed until death or 31 months. The dose of 875 and 1750 ppm was 2.5 and 5 times the threshold value of 350 ppm, respectively. Total tumor incidence in treated animals was similar to that in controls (Table 13-1).

TABLE 13-1. DOW STUDY

	Number of Animals		Total Neoplasms		Neoplasms minus Mammary Tumors	
Dosage	Male	Female	Male	Female	Male	Female
Control	189	189	200	561	183	240
875 ppm	91	92	77	246	67	71
1750 ppm	93	93	103	300	91	79

When tumors at each site were examined by tumor type, both benign and malignant, there were 8 differences between control and treated animals at the $p < 0.05$ level (Fischer Exact Probability Test). Decreased tumor incidence accounted for 7 of these differences; 1 was an increase in ovarian gradulosa cell tumors in females at a dose of 875 ppm. (No tumors were detected in 189 controls; 3 were detected in 33 treated at 875 ppm; and 2 were detected in 82 treated at 1750 ppm.) Since no pattern was consistent between those levels, and since 149 separate comparisons were made, $p = 0.05$ was not rigorous enough. The increases and decreases in tumor incidence were most likely due to random fluctuations.

The Dow study suffers from two (in the author's opinion, three) drawbacks. The first drawback is that animals were treated for only 12 months, rather than for a lifetime. Normally 18 to 24 months is the ideal time frame for a chronic study; a 12-month study cannot be called a "chronic" study. NCI does not use a 12-month protocol, and it is difficult (if not impossible) to compare results when animals are exposed for this short period. A second problem with the Dow study is the question of whether or not the MTD was used. Finally, this author considers as a third problem the fact that only one species was tested. NCI used both rats and mice, and the mice tended to be the more susceptible species. Finding no mouse carcinogenicity in the Dow experiments would possibly have indicated more strongly that MCF is not carcinogenic; no mice were included, however.

When compared to untreated animals, treated animals in the Dow study were no different in body weight, terminal organ weight, or mortality. The only sign of toxicity was an increased incidence of focal hepatocellular alterations in female rats at the highest dosage. Since treated rats showed little sign of toxicity, it is instructive to compare the dose to that in the NCI study, where only 3 percent of rats survived a 110-week study.

Comparison of Doses in NCI and Dow Studies

The dose in the NCI study was 750 and 1500 mg/kg, 5 days/week. The equivalent dose for male rats in the Dow study was 602 and 1204 mg/kg, 5 days/week. The calculations for these figures are as follows:

Dose was 875 and 1750 ppm, 6 hours/day, 5 days/week. To convert ppm to mg/m^3:

$$1.2 \times \frac{\text{mw comp}}{\text{mw air}}$$

$$1750 \times 1.2 \times \frac{133.5}{28.8} = 9734\ mg/m^3$$

To average the 6-hour exposure over a day:

$$9734\ mg/m^3 \times \frac{6\ \text{hours}}{4\ \text{hours}} = 2434\ mg/m^3/day$$

A 260-g rat breathes 111 ml air/minute, which is equivalent to:

$$\frac{111\ \text{cm}^3}{\text{minute}} \times \frac{60\ \text{minutes}}{\text{hour}} \times \frac{24\ \text{hours}}{\text{day}} \times \frac{1\ \text{m}^3}{10^6\text{cm}} = 0.16\ \text{m}^3/\text{day}$$

The amount of air breathed increases as $(\text{weight})^{2/3}$.

Dow rats (male) averaged 500 g. Therefore, the estimated amount that rats in the Dow study breathed is:

$$0.16\ \text{m}^3/\text{day} \times \frac{500}{260}\ 2/3 = 0.247\ \text{m}^3/\text{day}$$

Since a 500-g rat breathed 0.247 m^3/day of air containing 2434 mg/m^3/day, the dose rate was:

$$\frac{0.247\ \text{m}^3}{\text{day}} \times \frac{2434\ \text{mg}}{\text{m}^3/\text{day}} \times \frac{1}{0.5\ \text{kg}} = 1204\ \text{mg/kg/day}$$

Hence a dose by gavage of 750 mg/kg/day, 5 days/week, caused severe toxicity in the NCI study, but a dose by inhalation of 1204 mg/kg/day, 5 days/week, caused little or no toxicity in the Dow study. Perhaps MCF is less toxic by inhalation than by gavage, or perhaps a dose given at one point in time (gavage) is more toxic than a similar dose given over 6 hours (inhalation). Perhaps real strain differences in sensitivity do exist, or perhaps some technical problem caused the dose actually inahaled by rats in the Dow study to be less than intended. These alternative explanations should be explored, since the major route of human exposure is inhalation.

Lifetime equivalent doses, correcting for the fact that rats were exposed 5 of every 7 days and correcting for both the 18-month exposure in the NCI study and the 12-month exposure in the Dow study, are 402 and 804 mg/kg/day for the NCI study, and 215 and 430 mg/kg/day for the Dow study.

PPG Chemical Industries Study

EPA has also reviewed a study conducted for PPG Chemical Industries which was received on December 8, 1978 (Bell 1978). None of the exposure studies in this 1976 investigation meets the criteria for an oncogenicity study, and none of the submitted data are adequate for making an assessment of potential hazard and potential risk (Seifter 1979).

In a gavage study using dioxolane, PPG Industries found the MTD in drinking water to be 1 percent. Only 0.1 percent MCF was used, however, which does not meet the weight loss criterion. The depression of water consumption at 0.5 percent may have been due to systemic toxicity or (more likely) to objectionable taste (Seifter 1979).

CONCLUSIONS

While it points out the weaknesses of the Dow study, the report of the EPA Carcinogen Assessment Group contains weaknesses itself. The comparisons on page 7 of the report (NCI studies compared with the Dow study) have no meaning in the absence of pharmacokinetic data; and without tissue levels of MCF by the two routes of introduction into the organism, a statement in the report such as occurs on page 8 (bottom three lines) cannot be made (Seifter 1979).

The Dow study by Quast et al. (1978) is not a valid negative carcinogenicity result. The study did not meet the requirement of administering the MTD so that the animals exhibit unequivocal signs of toxicity (usually 10 percent less in body weight). Hepatocellular changes are not an established criterion for toxicity; they occur spontaneously without known treatment or exposure to vapors. The authors conclude that the changes "may" have been due to treatment (page 15). They also conclude that the incidence "may" have "possibly" increased (page 18). Such uncertainty is not solid support for the statement that the MTD was administered (Seifter 1979).

EPA is concerned with health effects of MCF, and will soon publish Section 4(f) of the TSCA Support Document for 1,1,1-Trichloroethane and the most recent data available on the subject. EPA appreciates the cooperation it has received from industry in the problem of MCF and MCF stabilizers.

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METHYL CHLOROFORM IN PERSPECTIVE

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INTRODUCTION

A number of specific issues must be addressed in discussing increased use of methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF) and its impact on stratospheric ozone (O_3) depletion. While the issue of the Conference on Methyl Chloroform and Other Halocarbon Pollutants is environmental, it is difficult not to discuss health effects when dealing with environmental impact, since the two areas are inherently linked. Surely, even very small concentrations of some chemical compounds are adverse to health.

Detrex applies MCF as well as the four other halocarbons in solvent vapor degreasing, a vital process that affects the metalworking output of the United States and the industrialized nations of the world. In the solvent vapor degreasing process, any particular industrial part or object may be dipped or agitated in solvent, or sprayed with solvent, as long as it is then subjected to boiling solvent vapor as the final step in cleaning. The virgin vapor contacts the object, condenses, and washes away soils.

In contrast, cold cleaning may take place in a cold (or even warm) condition; parts may be sprayed, dipped, or agitated in the solvent, but they are not subjected to boiling vapors. Certainly, use of MCF has grown significantly for cold cleaning as well as for solvent vapor degreasing.

Detrex pioneered solvent vapor degreasing in the U.S. 49 years ago through development of stabilizers for chlorinated hydrocarbon solvent and machines in which such solvents are used. Detrex was a large manufacturer of trichloroethylene (C_2HCl_3, TCE) and perchloroethylene (C_2Cl_4, PCE) from 1946 to 1972; though Detrex ceased all halocarbon manufacture in 1972, the company continues to sell substantial quantities of the five chlorinated hydrocarbon solvents for degreasing. Today, Detrex remains one of the largest U.S. manufacturers of solvent vapor degreasing machines; these machines employ all five of the chlorinated hydrocarbon solvents.

Detrex believes quite strongly that new State Implementation Plan (SIP) regulations must not force or induce substitution of MCF for TCE through application of rigorous rulemaking or reasonably available control technology (RACT) for TCE that does not place similar constraints on MCF. The company does agree with the position of the U.S. Environmental Protection Agency (EPA) that SIP's should require positive control of volatile organic chemical (VOC) emissions, including MCF. Unquestionably, all of these solvents, as well as methylene chloride (dichloromethane, CH_2Cl_2) and fluorocarbon-113 (CCl_2FCClF_2, FC-113), are valuable to industry.

The RACT concept is the proper and the responsible approach that, with coordination, should be applied at the same time and in the same manner to the three major chlorinated degreasing solvents — MCF, TCE, and PCE. MCF should not be exempt from regulation, and the user should not be induced or forced to substitute it for TCE or PCE, because a situation may be created that is more hazardous to the environment and population than now exists.

From an environmental standpoint, TCE breaks down in the troposphere within ~8 to 12 hours and PCE within ~48 hours, but tropospheric MCF is stable for roughly 8 to 10 yr. As shown in Table 4-4 of Singh et al. (this volume), the tropospheric residence time of MCF has been estimated by several investigators: 5 to 10 yr (Lovelock); 8 yr (McConnell and Schiff); 12 yr (Chang and Penner); 9 to 12 yr (Krasnec); ~6 yr (Rowland); 3 yr (Neely and Plonka); 10 yr (Crutzen and Fishman); 7 ± 1 yr and 8 to 11 yr (Singh). The present estimate of 8 to 10 yr is compatible with these estimates.

Until recently, the Clean Air Act (CAA) mandated chemical controls only within our troposphere. Prompted by new data on stratospheric O_3 and by the 1977 CAA Amendments, EPA clearly is directed to report and investigate depletion of stratospheric O_3.

TROPOSPHERIC PHOTOCHEMICAL OXIDATION VS. STRATOSPHERIC OZONE DEPLETION

Two reports are pertinent. To begin, EPA (U.S. Environmental Protection Agency 1979) concisely states the reasons for controlling photolytic materials or trying to reduce photochemical oxidation:

> Even at relatively low concentrations (in the troposphere) ozone has been shown to aggravate respiratory problems in sensitive individuals, to cause discomfort and interfere with normal breathing of healthy persons under conditions of stress. Controlled animal studies show ozone exposure has the potential for increasing the risk of respiratory infection and other long-term chronic effects...

In a second report (EPA Journal 1978), tropospheric photochemical oxidant problems are evaluated against stratospheric O_3 depletion problems. The report states concern over stratospheric O_3 depletion, and reference is made to aerosol can regulations. Next, the report states that reduction of this stratospheric O_3 could

> ...cause a substantial rise in the incidence of skin cancer. The layer of ozone now acts as a shield against biologically harmful ultraviolet radiation from the sun, and scientists fear that even a small percentage loss of this screen will have serious health effects around the world. In 1975 a Federal task force on the Inadvertent Modification of the Stratosphere [IMOS]...

and another group, the Interdepartmental Committee on Atmospheric Sciences (ICAS) of the National Science Foundation (NSF)

> ...warned that not only could skin cancers in humans increase but also other damaging biological and agricultural effects might occur.

A Coordinating Committee met in Bonn from November 28 through December 1 to review the O_3 layer situation on a worldwide basis.

Some of the figures quoted below are meaningful, because the deleterious effects from increases of O_3 and other photochemical oxidants in our troposphere can be related to those from reduction of stratospheric O_3.

> In 1976 a National Academy of Sciences (NAS) study, funded by EPA and several other agencies, had estimated that depletion of the world's ozone layer by fluorocarbons could range from 2 to 40 percent, with the most probable value at about 7 percent.

Actually, the upper limit estimated by NAS was ~20 percent, not 40 percent as indicated in this report.

> In December, 1977, in its report to the Congress pursuant to the Clean Air Act Amendments of 1977, NAS stated: 'As a result (of new knowledge) the estimated seriousness of...ozone reduction has been roughly doubled' to about 14 percent.

The general feeling now is that the level of reduction of stratospheric O_3 by fluorocarbons might be in the range of 14 to 17 percent — more precisely, 16 or 17 percent.

> More recently, a World Meteorological Organization symposium in Toronto last June heard fresh estimates by several experts of an 18 percent depletion. It is estimated that an increase of approximately 4 percent in the incidence of non-melanoma skin cancers among Caucasians is predicted for each 1 percent reduction in average ozone concentrations, with a disproportionately greater increase in cancer expected for higher percentages of reduction in ozone levels. Non-melanoma skin cancers rarely cause death but are considered serious and should not be neglected.

(Average O_3 concentrations are discussed later, to clarify what can be termed popular fallacies, myths, or misconceptions.)

People with fair complexions are more prone to skin cancer than the general population. Although basal or squamous cell carcinomas are not as deadly as melanoma, they cannot be considered innocuous.

> There are now about 300,000 cases of non-melanoma skin cancers annually in the United States, according to the National Cancer Institute [NCI]. If the currently estimated most probable ozone reduction value prevails, it implies more than 210,000 additional annual cases of non-melanoma skin cancer.

Next is a discussion of melanoma, an extraordinarily serious type of cancer that tends to metastasize. Incidence of fatality due to melanoma is somewhat analogous to that due to breast cancer in terms of rate of cure (or more appropriately, perhaps, lack of cure). Melanoma is very deadly.

> The incidence of melanoma, a much more serious disease, is about 1 to 3 percent (about 6,000 cases annually in the United States) of all skin cancers. Its cause may not be solely ultraviolet exposure, but this is considered a factor.

Evidence has been shown that skin cancers seem to prevail on those portions of the body most exposed to the sunlight. As was mentioned, the rate of incidence of melanoma in the United States is definitely increasing, and cancer authorities believe that melanoma is linked with ultraviolet-B (UV-B) radiation. NCI has confirmed that certain types of skin cancers, including melanoma, can occur because of excessive exposure to UV-B radiation.

> Depletion of the ozone layer also could cause other effects such as climate changes; effects to some plants and animal species; disturbances in aquatic and land ecological systems; alteration of the stability and effectiveness of farm chemicals such as pesticides and fertilizers; increases in eye cancer in livestock, and reduction in the yield of some crops, especially in areas of marginal production, according to the IMOS report.

Granted, the population could wear wide-brimmed hats, if so inclined, but could all of the animals and crops be covered with Mylar, a suggestion voiced recently? The effect on agriculture is a concern of extraordinarily serious nature. Photochemical oxidation is certainly noxious and should be reduced and eliminated where at all possible, but the solution of this problem must not create another of perhaps even greater magnitude. Considering the options, the better choice would be to have no significant reduction in stratospheric O_3 and to tolerate perhaps some increase in tropospheric O_3. Most experts in these areas probably agree with this statement.

RACT, RULE 66, AND METHYL CHLOROFORM

Forziati (this volume) has reported the various measurement tasks which have been assigned to predict the effects of O_3 depletion; these tasks involve modeling and monitoring UV-B radiation versus reductions in O_3, climatic effects, biological effects, health effects ranging from sunburn to melanoma, integrated assessments, and so forth. Further research in these areas is necessary, but a degree of understanding about O_3 depletion does currently exist. The ICAS Report (Atmospheric Sciences Interdepartmental Committee 1975) indicated that

> ...experiments exposing a variety of organisms including agricultural and wild plant species, phyto-plankton, insects, toad embryos and larvae to elevated UV-B irradiance have been made. Studies of whole organisms suggest that many are sensitive to UV-B radiation intensities now reaching the earth's surface. Avoidance of UV-B radiation and the use of molecular repair systems are important under present conditions. Many organisms have little reserve capacity to repair or to tolerate UV-B irradiation higher than that of current levels. Responses by different organisms exhibit a wide range of sensitivity.

While undoubtedly additional measurements should be performed, significant work already accomplished points to some very deleterious effects of O_3 depletion. The concept that Detrex espouses, and recommends to all of the regulatory agencies and government research agencies, is that photochemical oxidation in our troposphere must be limited; nevertheless, the limitations set must not create an even more serious problem by increasing stratospheric O_3 depletion.

Very simply, in solvent vapor degreasing, replacement of TCE (surely photolytic in the troposphere) by MCF (nonphotolytic in the troposphere) would allow very high escalation of O_3 depletion to continue. Unfortunately, the very resistance of MCF to tropospheric photolysis results in its long (8 to 10 yr) atmospheric residence time, permitting it to diffuse in all directions and to destroy stratospheric O_3. So, the substitution approach is an extraordinarily poor one, verging on irresponsibility. Users will be forced to substitute MCF for TCE because SIP's currently being prepared exempt MCF while controlling TCE by RACT. Instead, all chlorinated degreasing solvents should be controlled by RACT; the EPA guidelines procedure stressing control of all VOC's is the best approach.

If RACT is implemented for all of these solvents, all emission levels will be reduced substantially, and both stratospheric O_3 reduction as well as tropospheric O_3 formation (as related to these solvents) will be controlled. Indeed, accommodating RACT is relatively simple: the mere use of a cover (supplied by every manufacturer) on an open top degreaser will reduce emissions by at least 25 to 30 percent.

Simple, readily available control methods or technologies recommended by EPA for RACT are: chillers, carbon adsorption, higher freeboard ratios, mere replacement of the unit cover on top of the degreaser, and assurance that well-trained machine operators will successfully handle problems as they arise. These are straightforward, commonsense remedies that have significant impact on reducing emissions; RACT control in these areas is the appropriate logical or scientific choice over substitution of solvents in solvent vapor degreasers.

Rule 66 is the well known Los Angeles ordinance that was designed to reduce photochemical oxidation. Since Rule 66 originated in 1966, many other locations throughout the country have enacted similar ordinances. These adopted rules are rather onerous, involving stringent emission control to a maximum of 40 lb/day or less. Rule 66 regulations are so drastic that, given the alternatives of trying to meet them or substituting with an exempt solvent, the decision has invariably been to substitute with exempt solvents, including PCE, MCF, and FC-113. The great preponderance of substitution has been with MCF, and much less with fluorocarbons and PCE.

MCF has been the overwhelming substitute material for TCE because it can be used quite interchangeably with that chemical in the solvent vapor degreasing process. The vapor pressure of MCF is roughly twice that of TCE, but its boiling point is similar. Its solvency for the various soils on industrial parts to be cleaned is very close to that of TCE, and it can be used in the same machines as TCE (with some possible minor operating adjustments). All of these factors have been conducive to substitution. Because of Rule 66, then, the roles of the two solvents have reversed dramatically. Some years ago, TCE represented ~95 percent of all of the solvent usage in solvent vapor degreasing. Today MCF is by far the dominant solvent in solvent vapor degreasing.

In 1966, 4.82 x 10^8 lb of TCE were produced and emitted in the U.S. Since little or no chemical usage exists for TCE, the amount produced and sold is the amount emitted into the atmosphere. TCE production dropped to 2.92 x 10^8 lb in 1977, purely because of the restraints upon it.

The converse situation can be seen by a review of MCF production in the U.S. during this period. MCF production is also essentially synonymous with emission, except for a small amount (~4 to ~5 percent of total MCF produced) used in the manufacture of vinylidene chloride ($C_2H_2Cl_2$). In 1966, 2.43 x 10^8 lb of MCF were produced and essentially emitted; in 1977, 5.97 x 10^8 lb of MCF were emitted.

QUESTIONS AND MISCONCEPTIONS

In this section, major questions and misconceptions concerning stratospheric O_3 depletion are answered in order to clarify the MCF issues.

- If the O_3 layer varies naturally, why is its possible reduction by a few percent (or even 10 to 15 percent) by halocarbons and fluorohalocarbons of such concern?

Whatever the natural level and variations of O_3 are, if the annual average O_3 level across the globe is reduced a few percent, the world is extraordinarily impacted by increased UV-B radiation. Stratospheric O_3 is apparently running at a rather high level now: reduction may not appear to be a problem. But it must be borne in mind that the current fairly high level of sunspot activity is predicted to end in the early 1980's. At that time, a tremendous reduction in stratospheric O_3 may take place, causing international concern — concern that should be developed today.

- Why worry about a little change in UV-B radiation when exposure is greater as one approaches the equator?

The above argument answers this myth. The world is confronted by an average change, which is an extraordinary change.

- Placing MCF in degreasing machines as a substitute for TCE will produce lower emissions.

The vapor pressure of MCF is about twice that of TCE. The vapor pressure of MCF at 20° C is 104.5 mm Hg; for TCE, it is 57.8 mm. If there were an escape route in the machine for vapor, and the contents were idling and not boiling, chemistry and physics indicate that more MCF than TCE would be emitted to the atmosphere. However, either MCF or TCE at its boiling point would be at atmospheric pressure, and differences in loss would not be too significant.

- Little or no further substituting of MCF for TCE will take place if RACT is applied to TCE only, because MCF is more expensive than TCE.

The difference in cost between TCE and MCF is actually only a few cents per pound. The reversal in roles of these two solvents due to the substitution criterion during the past 12 yr indicates clearly that replacement will continue. Today in the U.S., some 2.9 to 3 x 10^8 lb of TCE are still being used in the solvent vapor degreasing process. If RACT control is applied to TCE while MCF remains exempt, MCF could be substituted for this remaining amount of TCE, meaning that another 3 x 10^8 lb of MCF would be emitted from the solvent vapor degreasing process.

- The Occupational Safety and Health Administration (OSHA) has published emissions limits, and if OSHA places a limit of 100 ppm on TCE, 350 ppm on MCF, 100 ppm on PCE, etc., obviously the emissions are controlled and the environment is protected. Why is any additional emissions control necessary?

The answer depends on the definition of the environment. Will it be defined as the surroundings of the worker, the plant as a whole, or ambient air? Consider the problems existing before the interagency groups began coordinating their functions; for example, to meet OSHA requirements for occupational exposure, the solvent vapor could merely be blown from the plant into the atmosphere by a high-volume exhaust fan.

- Nature has been coping with O_3-destroying processes for billions of years, and its self-balancing mechanisms have enabled the atmosphere to cope with change. Human activities are far too puny to seriously harm such a large and resilient system.

This myth is based on blind faith; nature is not infinite in its ability to overcome massive abuse, particularly in such an extraordinarily sensitive area as stratospheric O_3 depletion.

- More atmospheric data are necessary, as well as more advanced procedures; until more concrete evidence of O_3 depletion is gathered, preventive actions should be withheld.

The problem with this attitude is that action is deferred when action is indicated. More testing may certainly be desirable, but the real need here is to eliminate an exemption for a material which is clearly a hazard environmentally and toxicologically; MCF must be controlled by RACT, as well as TCE and PCE, the two other major compounds used in the solvent vapor degreasing process. Detrex supports continued use of all three solvents, but with reduction of all emissions through RACT.

CAPACITY AND PREDICTED USE OF METHYL CHLOROFORM

Although accurate production statistics exist for 1978, 1977, and 1976, the ~6 percent growth of MCF for the next 5 yr is somewhat confusing. Manufacturers have effected some massive increases in MCF capacity just recently, assuredly based upon solid reasons. In order for a chemical manufacturer to make a capital investment of from one to many millions of dollars, he must show that production will return sufficient money on the investment.

The 1976 worldwide capacity for TCE was 1.964×10^9 lb; usage was 54 percent of capacity, at 1.061×10^9 lb. In the same period of time, the worldwide capacity of MCF (with the exception of an unknown amount the USSR may have contributed) was 1.068×10^9 lb, 90 percent of capacity. This worldwide capacity was essentially emitted to the atmosphere.

Increases in the use of MCF worldwide have recently occurred, or will soon occur, because of new industrial capacities: 1.8×10^8 lb in Europe as of January 1977; 3×10^8 lb in Plaquemine, LA as of December 1977; 3×10^8 lb in Lake Charles, LA as of December 1978; and 1.4×10^8 lb in Geismar, LA in the near future. Since 1976, an additional 9.2×10^8 lb of MCF have become available worldwide — a growth in capacity of 86 percent. Such a great capacity investment is made only if a market exists for its utilization.

In the U.S. alone, capacity in 1976 was 6.4×10^8 lb. With the three new U.S. facilities mentioned above, the country will acquire an additional 7.4×10^8 lb in capacity by the end of this year. This 116-percent capacity growth is extraordinary for so short a period of time.

Singh et al. (this volume) have indicated the basic factors to be considered when reviewing the severity of a pollutant impacting stratospheric O_3 depletion: residence time in the troposphere, amount of emissions, and escalation of the emissions to the atmosphere. These components must be addressed when the need to apply RACT to MCF and to TCE is reviewed.

Most authorities agree that the residence time of MCF is ~8 to 10 yr. Moreover, the fantastic ballooning of MCF capacity will aggravate the emissions problem (and further large-scale capacity will undoubtedly be built).

The coatings industry emits 261×10^4 tons/yr of solvents to the atmosphere in the U.S. To date, coatings applications have not been prominent for MCF (the bulk of MCF is used in solvent cleaning). Should MCF be also exempted in coatings lines — which involve many operations, including textile, paper, and adhesive applications — use and emissions of MCF in these applications would be sharply escalated as well.

Many states are planning to exempt MCF in their SIP's, not only in solvent cleaning operations, but also in coatings lines. Detrex believes strongly that this approach is not responsible, but rather that MCF — along with TCE and the other chlorinated solvents — should be controlled by RACT. RACT is practical and involves simple procedures and controls readily available to users and manufacturers of solvent vapor degreasing equipment.

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DISCUSSION

Voice from Audience: Does Detrex do most of its business in PCE and TCE as related to MCF?

Mr. Schlossberg: We have a high volume of these chlorinated solvents but not a real stake in any one of them. Our purpose is to protect the solvent vapor degreasing process. We are one of the largest manufacturers of equipment used in this process. We are concerned with the possibility that TCE use may be eliminated, that PCE is under a cloud of carcinogenicity (which we don't agree with, incidentally), and now all of a sudden only the use of MCF remains unrestricted. Major producers are getting out of the TCE business, anticipating a point when only MCF can be used. As new data are acquired and when the boom gets lowered, it could wipe out the process. This, obviously, we don't want, because we want to continue to sell equipment for the process.

Dr. Mazaleski: I have one more question. Dr. Farber [Discussion, Lapp, this volume] stated, at least to my understanding, that health effects were not to be addressed here, but I would like to clarify this point. On October 29, 1978, Dr. Farber sent a letter to EPA, and he attached this document entitled, "1,1,1-Trichloroethylene as an Industrial Solvent: A Review of the Current Health Environmental Knowledge." In that document, which he wanted us to address, as we have really done, were mentioned the stratospheric O_3 problem and the health effects. I handled the health effects in part, and I could discuss these for about 4 days, if permitted. But Dr. Farber asked for that particular evaluation, and in Section 4, entitled, "Toxicity," he said "the most critical and definitive animal carcinogenicity testing for airborne contamination is by long-term chronic inhalation. A lifetime study was completed on male and female rats exposed to 1750 and 875 ppm of 1,1,1-trichloroethylene, up to 5 times the allowable 8-hour time, the weighted average outstanding. The results show the solvents to be noncarcinogenic in that test." Several EPA researchers have also addressed that issue very well, I think.

Mr. Schlossberg: I believe all the speakers at this conference were sent that package of information by Dow Chemical. Now, that did include the toxicological and environmental aspects of MCF use.

Dr. Hanst: I guess the issue that Dr. Farber was raising was with me: that the conference was getting off the track, and I had assured him that I didn't intend that we would go into the health issue in any great detail. I told him that I couldn't predict that some of the speakers wouldn't get into it, but it seemed to me the program was almost entirely on the atmospheric chemistry question.

Dr. Rowland: I want to paraphrase the question here. If we are going to have all this increased capacity, why are we going to have 6 percent increase in year-end production?

Dr. Farber: The 6 percent growth rate that I mentioned yesterday [Discussion, Neely and Agin, this volume] is based on analysis of the trends of the last 5 yr. This is what we expect. Six percent is not a small number in terms of absence of pounds. I am not minimizing the growth in terms of pounds. Six percent of a billion pounds is 60 million, and thus necessarily a small number. Six percent of the next year is a larger number. That is our estimate, and that is based on all the data I reviewed yesterday. We could both be wrong in our estimate. It could be less or more.

I mentioned yesterday that on a year-by-year basis we see fluctuations in that estimate of up to ±10 percent from a standard growth rate projected. In the last 5 yr of total 1,1,1 production, a decrease of ~5 percent can be found in one year of this sequence. That is a normal response to market demand, but I still anticipate no more than 6 percent average growth rate over the next 5 yr.

Now, somebody asked "Well, why do you go to capacity?" There are two reasons. First, the plant that we have used for producing TCE for about the last 30 yr is located in Shreveport. It is a very profitable product for us, and we are in the business to make money. Shreveport is the only plant we have in this country producing TCE and, as I told you yesterday, we have ~50+ percent of the 1,1,1 business. We obtained that business because we did all the groundwork for this business venture and decided to build that capacity. All right, that is in Texas. If we lose that plant because of Hurricane Carla, the stratospheric whatever, we have a fair share of our profits wiped out.

You build capacity for several reasons. One is anticipated growth. One of them is to have enough flexibility to make the product, if it is possible to do it that way, at two sites, not one. We also invested in a new TCE plant. As I said yesterday, I anticipate that we would be very happy to see 6 percent/yr (assuming, of course, that we are not harming the environment).

Mr. Schlossberg: Since I understood the question was asked of both me and Dr. Farber, I would also like to answer Dr. Rowland. As a businessman, I find it hard to understand that this huge capacity can be put on-stream without a firm expectation that there will be a home for it; unquestionably, there is going to be a driving force to use it, and the driving force is going to be to replace TCE and to get into the coatings markets, which are huge.

REGULATORY ISSUES INVOLVED IN HALOCARBON CONTROL UNDER THE CLEAN AIR ACT

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INTRODUCTION

This paper briefly identifies the regulatory issues and concerns involved in the control of halocarbons, specifically methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF), under the provisions of the Clean Air Act (CAA).

THE CLEAN AIR ACT

The CAA, as the primary legal mechanism for protecting ambient air quality, provides several regulatory options for control of substances identified as contributing to air pollution. The appropriate use of any of the CAA Sections depends on the nature, prevalence, and sources of a specific pollutant. Three areas of concern suggest regulation of MCF and other halocarbons by the CAA: (1) formation of ozone (O_3) in the troposphere; (2) depletion of O_3 in the stratosphere; and (3) direct danger to human health or welfare.

TROPOSPHERIC AND STRATOSPHERIC OZONE

Under Sections 108 and 109 of the CAA, National Ambient Air Quality Standards (NAAQS) are promulgated for O_3. Since this chemical is not emitted directly from controllable sources, the primary strategy for attaining the O_3 standard is control of volatile organic chemical (VOC) emissions that participate in photochemical reactions to yield O_3 in the lower atmosphere. Stationary sources of VOC's are controlled under State Implementation Plans (SIP's). In addition to the strategy of emission reduction, many SIP's and U.S. Environmental Protection Agency (EPA) guidelines utilize photochemical reactivity as a useful concept in reducing O_3 formation. The substitution of less-reactive for more-reactive compounds results in a lower net O_3. Incentive for the substitution of less-reactive VOC's is provided by exempting these materials from control or inventory requirements.

A large number of substances were originally exempted from control by solvent substitution provisions such as Los Angeles' Rule 66. Gradually, this number has declined as studies have shown that low- or moderate-reactivity VOC's may, under certain conditions, generate significant photochemical oxidant. In addition, concern over the potential of certain compounds for direct or indirect toxicity has led EPA to remove others from the list. EPA policy now recommends exemption for only four substances (methane (CH_4), ethane (C_2H_6), MCF, and fluorocarbon-113 (CCl_2FCClF_2, FC-113)); but EPA is concerned that similar health considerations may lead to the removal of MCF and FC-113.

The removal of MCF from the exempt list for environmental concerns other than photochemical reactivity would create an ironic situation in which this low-reactivity chemical must be inventoried and controlled to attain an O_3 level to which it contributes only negligibly. Maintaining it on the list, however, endorses uncontrolled substitution of MCF for nonexempt chemicals, though key health questions remain unresolved. Although many scientists may agree that MCF contributes in only a very minor way to tropospheric concentrations of O_3, for EPA to continue advocating the substitution of this high-volume solvent is clearly inappropriate, as scientific evidence suggests that the resulting increase in MCF emissions may (1) contribute significantly to stratospheric O_3 depletion, or (2) present a direct risk to human health.

Under the CAA Amendments of 1977, EPA is given specific authority to protect the stratospheric O_3 layer. In view of the predicted long lag between emission of fully halogenated pollutants and their interaction with O_3 in the stratosphere, a precautionary stance on the part of EPA is appropriate. Though considerable uncertainty and disagreement exist over the impact of non-fully-halogenated species (such as MCF) on the O_3 layer, EPA does not conclude that this growing source of atmospheric Cl can be ignored in the absence of additional information. The exchange of ideas and the identification of research needs permitted by the Conference on Methyl Chloroform and Other Halocarbon Pollutants is thus strongly supported by EPA.

Aside from the indirect effects to health that halocarbon pollutants may induce through tropospheric O_3 formation and stratospheric O_3 depletion, EPA must consider the direct hazards of toxicity, mutagenicity, carcinogenicity, and teratogenicity. There is evidence (albeit controvertible) of mutagenicity in bacterial and mammalian test systems due to MCF. This circumstance raises the possibility of human mutagenicity and/or carcinogenicity and has led EPA's Carcinogen Assessment Group to conclude that "suggestive" evidence of human carcinogenicity exists for this chemical.

REGULATION OF METHYL CHLOROFORM

Part B of the CAA, which addresses protection of the O_3 layer, states that pollutants judged to endanger public health may be regulated under Sections 108 and 109 (NAAQS); Sections 111 and 111(d) (Standards of Performance for New Stationary Sources); or, if the effect is "serious and irreversible" or "incapacitating and reversible," under Section 112 (National Emission Standards for Hazardous Air Pollutants).

At the present time, two regulatory approaches have been recommended for MCF:

(1) Deletion of MCF from the recommended list of exempt solvents, perhaps leading to controls under SIP's for the O_3 standard.

(2) Regulation of MCF under Sections 111 and 111(d) as a solvent in the metal cleaning industry.

The reasons for considering the deletion of a low-reactivity substance from the exempt list — i.e., potential for direct and indirect health effects, and substantial emissions — also apply to regulation of MCF in the solvent metal cleaning industry under Sections 111 and 111(d).

Section 111, Standards of Performance for New Stationary Sources, provides control, through emission standards, of new pollutant source categories listed under Section 108. As precursors to the listed pollutant O_3, reactive hydrocarbons emitted from such sources as vapor phase degreasers will be regulated in this manner. In addition, MCF and four other halocarbon solvents (trichloroethylene (C_2HCl_3, TCE), perchloroethylene (C_2Cl_4, PCE), FC-113, and methylene chloride (dichloromethane, CH_2Cl_2)) will be designated under Section 111(d). Thus, emissions from both new and existing solvent metal cleaners that use these five compounds will be regulated.

The decisions to proceed with regulatory controls for MCF have been based on rather inconclusive scientific data. Inferences drawn from these data are subject to uncertainty, particularly in view of conflicting results by other investigators; EPA continues to seek the resolution of this uncertainty. However, EPA is convinced that present evidence, as well as the magnitude of projected emissions and the persistence in the environment that would result from continued, uncontrolled use of MCF, dictate caution in policies and regulations that might encourage significant increases in public exposures.

DISCUSSION

Dr. Rowland: As I understand, one reason you advocate the deletion of MCF from the list of exempt solvents is the possibility that it depletes stratospheric O_3. If that is correct, surely you must be also asking for deletion of FC-113, where the effect must be 5 to 7 times greater?

Mr. Kellam: Yes, we are.

Dr. Klauder: As you know well, the chlorofluorocarbon regulation was unique because a generic class of chemicals was regulated. At the first regulatory meetings where regulatory scope was discussed, this concept was considered foreign. There was strong support for a regulation that would apply only to fluorocarbon-11 (trichlorofluoromethane, CCl_3F, FC-11) and fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2, FC-12). In subsequent meetings, it became quite apparent that if the regulations governed only FC-11 and FC-12, substitution of FC-113, fluorocarbon-114 ($CClF_2CClF_2$, FC-114), and other fully halogenated chlorofluoroalkanes might lead to a noneffective regulation.

I have the same concern with the approach you have presented. As Mr. Schlossberg told us, regulation of TCE resulted in a great increase in MCF. Now you propose to control MCF, FC-113, and perhaps a few of the other halocarbons. Shouldn't this problem be addressed on a generic basis? Are we going to be in a position, 5 yr from now, where we will have conversion to other chlorinated and brominated halocarbons? It may be worth taking additional time to adequately address the entire problem of chlorinated and brominated halocarbons.

I agree with Herbert Wiser (and have stated to EPA several times, myself) that we may be talking about all halocarbons on a continuum of reactivity. At one end, we are talking about very reactive compounds which are involved in tropospheric photochemical reactions. At the other end, we are talking about very nonreactive compounds which migrate upwards, causing stratospheric O_3 depletion. All of the brominated and chlorinated halocarbons fall somewhere on this continuum. This seems to be a problem that must be addressed in a generic fashion and for which acceptable burdens of Cl and Br in the stratosphere must be determined.

Mr. Kellam: Initially, the CAA did not specifically provide for generic regulations under Section 111. However, the 1977 CAA Amendments have allowed us some latitude in developing these kinds of controls. We have an ongoing program, the Synthetic Organic Chemical Manufacturing Industry Program, which, in a broader context, is intended to develop technological guidelines for implementing generic control technology for an entire industry. These regulations take account of your concerns regarding stratospheric O_3, as well as EPA's concerns about formation of tropospheric O_3. The intention is to develop regulations broad enough to apply to most types of source categories within the organic chemicals industry. Of course, these regulations will take into account technological feasibility, as well as the cost of control.

Dr. Humenny: With the recommendation that MCF be controlled, will it be subject to New Source review or an offset requirement?

Mr. Kellam: I would assume the deletion from the exempt list would put MCF into the same category as all the other nonexempt chemicals. How a specific state wishes to handle the controls and requirements within the EPA guidelines, I believe, is at the State's discretion, and will depend on how its SIP is designed.

There is one other point that Mr. Schlossberg brought up in referring to an August 24 memorandum of Walt Barber. His comment was that Mr. Barber was essentially saying that, although we were considering the deletion of MCF from the list of exempt solvents, we would not disapprove SIP's continuing to exempt these solvents. I would like to clarify the context of that memorandum, because I believe there is an important element of timing in what Mr. Barber was saying. He says:

> I recognize that many States are well along in the preparation of their regulatory packages and inventories. In order not to change the existing guidance at this late date, I am requesting that you advise your State Directors that, although

> we will not disapprove the State oxidant SIP submittal which exempts methyl chloroform from control, we are very concerned with the environmental risks associated with widescale substitution to methyl chloroform; and that the uncontrolled use of methyl chloroform as an approved means for compliance should be avoided wherever possible.

I think his intent was to apprise the states of our concerns without disrupting the SIP revision process, which was in its final stage in August.

Mr. Schlossberg: I do agree with exactly what you said, but what I was trying to convey was the information that you were getting from the states as they interpreted that number. I know what Mr. Barber had in mind, and his action was forthright.

Dr. Rowland: Who has superseding jurisdictions, the states or the federal government, in removal from the exempt list and approval of the SIP's?

Mr. Kellam: In the case of the O_3 standard, EPA does have approval authority of the SIP. There is an outside possibility, if MCF were removed from the exempt list, that EPA could disapprove SIP's based on its continued exemption. In this case, the state would have to rewrite the plan, or I think the CAA would allow EPA to actually promulgate a plan for the state, if we couldn't reach some agreement.

INTERAGENCY WORK GROUP ACTIVITIES ON NONAEROSOL USES OF CHLOROFLUOROCARBONS

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Washington, D. C.

INTRODUCTION

The Chlorofluorocarbon Interagency Work Group has been formed to regulate the reduction of chlorofluorocarbon (fully halogenated chlorofluoromethanes) emissions. For a clearer perspective on the Work Group's present activities, a brief history is given below.

THE CHLOROFLUOROCARBON PROBLEM

The effects of chlorofluorocarbons (CFC's) on depleting stratospheric ozone (O_3) came to light at the beginning of this decade. The early 1970's brought the supersonic transport (SST) and questions concerning effects of nitrogen oxides (NO_x) emitted from high-flying aircraft. Scientists also questioned whether damage to the O_3 layer could come from other chemical compounds. In 1974 Drs. Rowland and Molina presented a paper detailing the CFC O_3 depletion hypothesis. Their findings mobilized the Council on Environmental Quality (CEQ) and the Federal Council on Science and Technology to initiate additional studies on CFC emissions. Thus, the Interagency Task Force on the Inadvertent Modification of the Stratosphere (IMOS) was formed. In 1975 this Task Force reported that cause for concern existed with regard to CFC emissions, and that, if the National Academy of Sciences (NAS) confirmed their study, federal regulatory agencies should initiate rulemaking procedures to restrict CFC uses.

With the fall 1976 publication of the NAS report confirming the threat to the O_3 layer from CFC releases, the Food and Drug Administration (FDA), Consumer Product Safety Commission (CPSC), and Environmental Protection Agency (EPA) began to consider action against the use of CFC's in products under their respective jurisdictions. By the end of November 1976, CEQ had already held several meetings to coordinate regulatory activities, thus establishing the first CFC Interagency Work Group. FDA, CPSC, and EPA were designated as the lead agencies, but were aligned with CEQ, the National Aeronautics and Space Administration (NASA), National Science Foundation (NSF), National Oceanographic and Atmospheric Administration (NOAA), Department of Commerce (DOC), and Department of Transportation (DOT).

The Work Group acknowledged that EPA had the broadest authority over CFC's under the new Toxic Substances Control Act (TSCA) enacted in October 1976 and also the longest-term interest in CFC regulation; therefore, EPA was given the leadership role. Moreover, the members concluded that individual legislation by CPSC, EPA, and FDA was unnecessary, since all aerosol uses could probably be regulated under TSCA and the Federal Food, Drug, and Cosmetics Act.

PHASE I

The Work Group's initial plans called for division of the CFC program into two phases. The first phase would be the regulation of CFC's used as aerosol propellants. The second phase of the regulatory process would be the investigation of all other uses of CFC's.

Continuous Work Group deliberations had revealed many issues and suggested approaches regarding proposed regulation of aerosols. Some key issues included definition of the compounds to be regulated; definition of "aerosol propellant;" timing of regulation enactment; and consideration of CFC production and recovery requirements as regulatory alternatives. The resolution of these and other problems necessitated dividing the Work Group into subcommittees in order to review existing data and recommend solutions.

The question of which products should be exempt from regulation became an important issue during the Work Group meetings. After numerous discussions, this problem was resolved by subjecting each aerosol product to the four basic questions below to determine if the product was essential and therefore exempt from regulation:

(1) Are alternatives available?

(2) What is the economic significance of the product, including effects in the marketplace?

(3) What are the environmental and health impacts of the product and its alternatives?

(4) What are the effects on quality of life if the product becomes no longer available for use?

After evaluating scientific reports, analyzing economic impacts, and receiving testimony from meetings with the American public and businesses, the Work Group recognized that uncertainties about the magnitude of O_3 depletion did not override concerns for public health. The available data indicated that to further delay regulation would in itself lead to unreasonable risks to long-term human health and the environment. Further, the nonessentiality of most aerosol products, plus the ready availability of substitutes for aerosol propellants, supported the EPA and FDA decision to proceed on March 17, 1978 with a ban on manufacturing and processing of CFC's for use as aerosol propellants.

Since October 15, 1978, all manufacturing of CFC's for aerosol propellant use has been prohibited. Since December 15, 1978, all processing (including processing for export) and distribution of CFC's for use in aerosol products has been prohibited in the U.S.; import of products containing CFC's and the manufacturing and packaging of food, drugs, or cosmetic aerosol products containing CFC's were also banned as of that date. On April 15, 1979, food, drug, and cosmetic aerosol products containing CFC's may no longer be introduced into interstate commerce in the U.S. All finished products already on the market and in distribution channels, however, can be sold until stocks are depleted.

Both EPA and FDA regulations identified certain aerosol products as exempt products. EPA exempted Department of Defense products, electronic cleaners, aircraft maintenance products, mine warning devices, plastic mold release agent products, diamond grit spray, and some pesticide products. FDA exempted certain metered dose drug products used for oral inhalation and contraceptive foam products. Exempted uses, however, account for only 2 to 3 percent of total CFC aerosol uses in the U.S. The ban on nonessential aerosol uses of CFC's is expected to yield a reduction in annual U.S. CFC emissions of >60 percent.

PHASE II

Because regulation of aerosol uses may not be sufficient to reduce CFC emissions, and because of the growing uses of CFC's in nonaerosol applications, attention has now focused on domestic nonaerosol emission sources. The purpose of Phase II is to more accurately define current and future levels of CFC emissions from nonaerosol uses (such as refrigerators and air conditioners) and to evaluate means of achieving further emission reduction with regard to socioeconomic consequences.

In many respects, Phase II is a continuation of Phase I. Because no single legislative statute administered by EPA, FDA, and CPSC provides jurisdiction over all products that utilize CFC's, collective evaluation by these agencies is still the preferred approach. But continuation of Work Group activities does not necessarily indicate additional regulation — at present, the Group remains in a fact-finding mode.

In August 1977 Congress passed the Clean Air Act (CAA) Amendments, which specifically charge EPA with protecting the stratosphere (especially its O_3). However, the regulation banning CFC-propelled aerosol products was enacted under TSCA, since Phase I investigations began under TSCA. The passage of the

1977 CAA Amendments thus brings into question the legislative authority under which any future regulations will be enacted.

In answer to this question, the CAA Amendments strongly suggest that any future action to protect the stratosphere be taken under their provisions. However, the Amendments specifically state that new statutory provisions are not to affect any proposed rule published under TSCA prior to enactment of the Amendments, nor any state law or regulation pertaining to control of halocarbon propellants in aerosol sprays.

Part B of Title I of the CAA Amendments directs the Administrator of EPA to determine human effects on the stratosphere by conducting and coordinating research and monitoring studies undertaken throughout the government, universities, and the private sector. This section also authorizes the Administrator to control any substance, practice, process, or activity reasonably anticipated to affect the stratosphere, especially the O_3, if such effect is reasonably anticipated to endanger public health or welfare. In both cases, the Administrator is required to report to Congress on specific dates the results of research findings, progress on international cooperation, and results of regulatory activity by EPA and other federal agencies regarding protection of the stratosphere. Congress is also to receive recommendations for additional research.

Because of these new Amendments, questions have arisen regarding the breadth of the Work Group's activities. Should the scope broaden to include all chemicals suspected of being harmful to the stratosphere, or should the focus be solely on CFC's? Because of limited or nonexistent facts concerning harmful effects of other suspected O_3 depletors necessitating regulatory consideration, the Work Group continues to concentrate on CFC emissions. Nonetheless, other chemicals have been at least discussed by the Work Group; EPA will need to conduct and support more research to confirm suspicions of harmful effects from such chemicals in the stratosphere before initiating regulatory action and convening a Work Group, however.

The immediate task before the CFC Work Group is to gather information on nonaerosol uses of CFC's. Included in this category for review are CFC's used in refrigerators and air conditioners, as foam-blowing agents in the manufacture of urethane and nonurethane foams, and as cleaning agents in the solvent industries. A host of miscellaneous minor uses will also be reviewed. Chlorofluorocarbons used in these applications are rarely consumed, although minor amounts may be chemically or thermally broken down. With the exception of certain products such as flexible urethane foam, CFC's are released from most nonaerosol products over long periods of time (sometimes over 20 yr after manufacture).

The Work Group is examining ways to eliminate or minimize CFC emissions. This review extends to the best available technologies, including reuse, recycling, and other traditional types of control. These approaches specify performance standards required to reduce emissions or, in some cases, a complete ban on a product. The latter strategy was adopted for the current regulation of aerosol uses of CFC's.

The Work Group is also examining nontraditional control options, including marketable permits, production ceilings, emission fees, and voluntary measures. As an example, emission fees could be added to the price of a substance under scrutiny to discourage its use. Another possible option is a system of marketable permits, entailing an "auction," after a total maximum level of CFC emissions has been set, of "rights" to emit certain amounts of CFC's within that level. In both cases, the marketplace — not the government — would determine which products are essential.

Substitutes for CFC's in nonaerosol products are also under evaluation, although few substitutes for CFC's appear available at the moment. In addition, as substitutes are evaluated, caution is exercised that the substitutes do not themselves create health or environmental problems.

The Work Group is looking at the entire life cycle of each product containing CFC's — manufacture, normal use and servicing, and finally disposal. Emission profiles are evolving that show where greatest emissions occur.

Within the air-conditioning and refrigeration category, for instance, the largest source of emissions appears to be mobile air conditioners. In 1976, emissions from this source amounted to 74 million lb (73 percent of the total 103 million lb emitted from all air-conditioning and refrigeration units); by 1990, mobile air-conditioning emissions are expected to rise to 113 million lb (77 percent of the total 148 million lb for this category). Further analysis indicates that most emissions occur as a result of leakage, recharging, and servicing.

Another category, plastic foams, includes three types of products: flexible urethanes, rigid urethanes, and nonurethanes. Flexible or soft foams are used as cushioning in furniture and automobiles. During the manufacture of flexible urethane foam, CFC's pass through the product, helping form the cells of the foam, and are immediately released into the atmosphere. On the other hand, emissions during manufacture of rigid urethanes (used primarily as insulation) are small, because the insulating efficiency of rigid foam depends on retention of CFC's. But these CFC's slowly leak into the atmosphere over the life of the product, creating an emissions problem during normal use and disposal. The third type of foam, nonurethane, includes mostly polystyrenes and polyolefins used primarily for food and other packaging. Manufacturing emissions from these products resemble those from flexible foam. Moreover, since the length of service of these products is very short — perhaps several weeks before disposal — emissions are considered to be immediate.

The estimated total amount of emissions from flexible, rigid, and nonurethane foams for 1977 is 79 million lb, an amount slightly less than the 103 million lb released from all air-conditioning and refrigeration units. However, the use of foams is growing to the extent that, by 1990, emissions are projected to be more than 200 million lb and will likely exceed emissions from air conditioning and refrigeration. Hopefully, emission profiles from these and other products under investigation will help identify stages of maximum possible emission reduction with least impact on both product performance and the economy.

ADDITIONAL RESEARCH

Helping the Work Group to collect and analyze data are research organizations such as the Rand Corporation, SRI International, the University of Maryland, and NAS. The Rand Corporation is analyzing the economic feasibility and impacts of alternative regulatory options. This study, supported by EPA, CPSC, and FDA, has received input from the Work Group regarding the scope of work and regulatory approaches to be analyzed.

Under the direction of EPA's Office of Research and Development, research teams at the University of Maryland and SRI International are analyzing tradeoffs between the costs and benefits of additional CFC control. As mandated in CAA, NAS is preparing a comprehensive report on causes, effects, and alternative methods of control of stratospheric O_3 depletion. One goal of this study is to update the latest developments in atmospheric chemistry of stratospheric modification.

EPA will use data collected in these and other investigations to conduct its own study of the levels associated with nonaerosol uses of CFC's. This risk-assessment report is expected to provide quantitative estimates of the impact of uncontrolled future emissions on O_3 levels, as well as the reduction of these effects resulting from selected control options. This report should identify (among other things) baseline emission scenarios and emission reduction scenarios for CFC's and then correlate both with quantifiable health and environmental risks.

In the coming months, the Work Group will review these and other reports and analyze various control options in order to develop recommendations on additional regulatory needs. Where appropriate, these recommendations will be categorized by specific industry and by individual consumer product. Division of the Work Group into subcommittees by industrial category will provide the maximal response to differences in emissions control. Assuming current studies are completed as planned, the Work Group expects to present a regulation policy for chemicals in question to the respective Agency Heads by the end of 1979.

FINAL COMMENTS

Examining the need for more regulation is within the Work Group's phased-approach philosophy to controlling CFC's and acknowledges the need to carefully balance risks and benefits associated with nonaerosol uses. During the deliberations on aerosol uses, the Work Group developed regulations even though uncertainties related to the risk of CFC's were not resolved, because substitutes were readily available. In the case of nonaerosol uses, however, action against the continued use of these products could have a much greater impact on the U.S. economy and well-being.

Preliminary reports indicate large investments may be necessary to reduce CFC emissions from nonaerosol products. An obvious stumbling block faces the Work Group — the need to curtail essential nonaerosol emissions while use of nonessential aerosol products continues worldwide.

At the international meeting on CFC's in Munich, Germany in December 1978, the U.S. delegation headed by Barbara Blum, Deputy Administrator of EPA, urged those in attendance to take a unified global approach to reduce CFC emissions from aerosol products. Although member nations resolved that all countries should significantly reduce CFC emissions and continue studies on the technical and economic aspects of the CFC question, firm commitments by other countries did not materialize. While the Work Group will continue its efforts in the international community to achieve worldwide control of CFC emissions, the present international situation is of concern to the Group.

The role of the CFC Interagency Work Group becomes one of delicately balancing all scientific and economic factors to produce a viable, reasonable position. The Group looks to the scientist to continue his research in providing necessary information, and to the industrialist to continue his search for new methods to control CFC emissions and to improve the efficiency of present emission reduction methods. If all factions of society work together, the relevant scientific, socioeconomic, and legal aspects of the CFC issue can be carefully reviewed so that this Interagency Work Group can make the best recommendation on future regulation needs.

DISCUSSION

Dr. Sobolev: I have two questions. As I understood, Mrs. Bishop, the CFC Work Group was established by CEQ.

Mrs. Bishop: I think what happened in those early days was that CEQ became aware of the efforts of FDA and others to consider regulatory action against CFC, and these actions necessitated that agency representatives be called together to share information and regulatory approaches.

Dr. Sobolev: I am truly interested in the legal aspect. They initiated information on your Group. What part of EPA, what agency, could dissolve the Group, if a need for that became justified? I know now who has the authority to form your Group. Who has the authority to dissolve it?

Mrs. Bishop: Let me rephrase. This isn't a question of authority. The purpose of CEQ, as I understand it, was to coordinate programs in different agencies. I will also defer to some of our veteran Work Group members here who could shed more light on what happened in the early days of Work Group activities.

Dr. Sobolev: I will wait for that answer. Perhaps you could answer my second question. Not too long ago, NAS decided that, in view of some new measurements of rate constants, NO_x from SST's were no longer considered likely to pose a significant environmental hazard. Suppose, as a result of future developments, NAS comes to similar conclusions regarding Cl from fluorocarbons. What would happen to your Group? Would it just keep going?

Mrs. Bishop: Well, we are currently studying the CFC question and whether we should pursue it further.

Dr. Sobolev: That is only because NAS decided that there was cause for concern, that fluorocarbons are an environmental hazard. Suppose NAS —

Mrs. Bishop: Came up with a reversed decision?

Dr. Sobolev: Yes.

Mrs. Bishop: Then I would like to think, and Dr. Wiser can correct me, that EPA would probably reverse the regulation.

Dr. Sobolev: I wasn't even thinking that far. I was just thinking of what would happen to your Group. What agency would have the authority to say that the services of your Group are no longer needed?

Mrs. Bishop: When EPA decides to initiate a regulation, a work group is convened to develop this regulation. If there were a need to eliminate a regulation, although I don't know whether that has happened, a work group would probably convene to do the reverse and proceed through EPA with prepared documents indicating this regulation is not needed.

Dr. Sobolev: Please forgive me. I am not trying to be funny or sarcastic. I just wanted to know what would happen.

Mrs. Bishop: You are asking a question on doing something in reverse in EPA that may not have been done before, and it is probably a good question. My answer is just my opinion.

Dr. Sobolev: Thank you.

Dr. Wiser: I would like to add to that and clarify some of the historical misconceptions presented here. These committees are not established by law. The various agencies thought it would be very efficient — since we are all looking at the same scientific data, in many areas — to work together. We did. We hope to continue to work that way. Most of these committees, regardless of the length of their existence, are ad hoc committees, and when a problem goes away, the committee members are assigned to other positions, and the committees are dissolved. Furthermore, although NAS is a very creditable body and, based on NAS expertise, does present an overall, latest, state-of-the-art summary with recommendations for scientific research needs for regulatory action, etc., these are not the only documents that are reviewed and studied by the agencies. We study virtually everything that comes to our attention in the published literature.

Mrs. Bishop: Thank you for reinforcing that.

PANEL DISCUSSION

Dr. Schiff: I was asked to chair this session, perhaps because of my notoriety as an author. I authored a paper on methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3, MCF) which was misinterpreted in certain quarters as an attack on the U.S. Environmental Protection Agency (EPA), and I would like to deny that as the intent. I was also coauthor of a book which was interpreted as an attack on almost everybody, which I, of course, totally deny! However, I will attempt to maintain this image to inject a little bit of controversy here.

The advice I would give EPA is not to be convinced by industry that MCF emission is probably okay because it is removed in the troposphere. Neither should EPA be convinced, on the other hand, by scientists who say that everything must be known about tropospheric chemistry, about the hydroxyl radical (OH) concentrations, about the N/S ratios, etc., and who seek more research support. Such a research effort is very commendable but not absolutely the first required task.

The amount of any substance, including MCF, entering the stratosphere is undoubtedly proportional to the amount in the troposphere, and tropospheric MCF measurements are ~100 ppt. To estimate the stratospheric effect of MCF relative to fluorocarbons, the relative tropospheric concentrations can be used. This ratio provides an approximate measure of the relative effects of these substances on the ozone (O_3) layer. The present tropospheric concentration ratio of MCF to fluorocarbon-11 (trichlorofluoromethane, CCl_3F, FC-11) plus fluorocarbon-12 (dichlorodifluoromethane, CCl_2F_2, FC-12) is about 1 to 4.

The projected time when MCF concentrations will demand serious concern is the point when these concentrations contribute approximately the same amount of Cl as do present FC-11 and FC-12 concentrations. Using Professor Rowland's figure of 1.1 percent/month increase (provided present emission rates remain fairly constant) and multiplying that figure by 1/4, one arrives at a projected time of ~10 yr for stratospheric Cl contributions of MCF to parallel those of FC-11 and FC-12. On the other hand, using Dr. Rasmussen's estimated increase rate over the last year yields a different number. The most important issue to be addressed appears to be the status of MCF measurements. How well do we know its concentrations, and what are the uncertainties? Correlatively, how well can we calculate for the absolute amounts we want to know? The several inconsistent findings reported here give rise to confusion. Some people have not formally presented their MCF measurement methods, and these contain further inconsistencies needing clarification. Other groups, including the National Center for Atmospheric Research (NCAR) and the National Oceanographic and Atmospheric Administration (NOAA), have suggested strongly that MCF cannot be measured with any degree of accuracy. A few do not believe any good absolute measurements have been made. Jim Lovelock suggests that great difficulties exist in obtaining MCF measurements, yet Professor Rowland observes few measurement difficulties.

The question of precision versus accuracy must also be considered. Precision was not examined thoroughly in the presentations and discussions at this meeting. Inconsistencies were rather ignored. For instance, Dr. Rasmussen, is it not correct that you have made surface measurements and measurements from the airplane, and you find differences between ground measurements and measurements in the air? Let me hold the question for the time being and return to you for a response.

If you use real-time measures, sampling directly into a gas chromatograph on an aircraft, and do a latitude sweep, the absolute numbers may be questioned, but the relative measurements are usually accepted. We have seen different latitude dependencies on the same aircraft.

Dr. Crutzen, I would like you to comment again on that latitude curve from the NCAR group where a very strong latitude dependence peaks at about 50° N, revealing a very strong latitude dependence in the Northern Hemisphere (NH) and virtually none across the interhemispheric zone. In contrast, other slides showed the two hemispheres to be fairly uniform and a discontinuity to exist across the hemisphere. These questions should be addressed by the people in this room who were involved in the measurements. Dr. Rasmussen, why don't you start off?

Dr. Rasmussen: Well, three questions are to be answered. One, can we or can we not measure MCF? In automated, routine gas chromatographic analysis, we use 5-ml ambient air samples to determine specific halocarbon concentrations, as resolved on a silicone oil column. A particular peak can be verified as MCF by running the sample on dissimilar columns with dissimilar substrates and differential retention times; and classic gas chromatographic technology will confirm that it is, in fact, MCF. As you heard yesterday, in the urban environment, some contamination with ethylene dichloride ($ClCH_2CH_2Cl$) is possible. However, in the true rural situation, nothing has ever been observed underneath the MCF except MCF. This scale can be expanded to direct analysis, and the same amount of MCF is measured. The precision of analysis is evident again and again and again; it is something on the order of ±1.2 ppt. So the answer to the first question is "Yes, we can measure MCF." We use the same technology used successfully in other laboratories. In the primary standards we have been using for ~4 yr, the change in MCF has been no more than ~±4 or 5 ppt over a period of time. It is a random change, and it has no directional drift. So I feel quite confident that we can measure MCF.

I would also like to respond to your comment regarding the differences between our ground measurements and measurements in air. Joe Krasnec and I collaborated on the GAMETAG flight, and our different results on the same flight, I feel, reflect some analytical difficulties caused by operating a gas chromatograph on an aircraft. We prototyped together on two different Learjet flights, one in 1975 and one in 1976. He ran the system in a Convair 990, and the original work demonstrated it was impossible to get the precision of analysis with the airborne instrument that could be achieved in carefully collected paired samples. Only time and effort will resolve the true discrepancy in our values from the 1978 GAMETAG flight across the Pacific.

The second question is: "How accurately can we measure MCF?" The technicians in my laboratory, Peter Simmons, Jim Lovelock, and I have found agreement on ambient values, the precision at those ambient concentrations, and an estimate, our best professional judgment, of the absolute accuracy of the standard. During the entire summer of 1975, several people, including Joe Krasnec, intensively prepared dilution standards of these compounds, both by permeation tubes and with static pollution. We perpetuated these values from the fall of 1975 to the present. We did more work on the primary calibrations, in at least three informal and one formal interlaboratory calibration, encompassing ~25 laboratories. These scientists are experienced in making halocarbon measurements, and we agree very well. Our laboratory and Lovelock's laboratory agree within ~5 percent on most of the exchanges. This might be considered collusion, because we intercalibrate so often, but we agree within a few percent; with NOAA's laboratory now and Kirby Hensen's group —

Dr. Schiff: On MCF?

Dr. Rasmussen: Excuse me, on the fluorocarbons. On MCF the agreement is maybe within ±10 percent. No significant difference in MCF values was found between my laboratory and Paul Golden's laboratory at NOAA. A discrepancy arose between Leroy Heidt's measurements and ours in 1977 in a very intensive set of precalibration exercises, when GAMETAG first started.

Dr. Schiff: Why does the Golden group submit they cannot make a standard sample of MCF or keep it for any length of time, and are unable to get a correlation calibration of standard with Leroy Heidt? We were told this yesterday.

Dr. Rasmussen: That is news to me. Paul Golden is in Germany; when he returns, I will discuss the standard with him.

In a few days, preparation and packaging in our laboratory will be completed of calibration samples in exceedingly clean, highly polished, passivated stainless steel bottles. The samples will be sent to 12 participating laboratories with a concentration standard of dissimilar concentration, a checklist on exactly how and where the samples are run, and a request that the samples be run on 2 separate days by either the same analyst or a separate analyst. Reproducibility will be evaluated. We will have the conditions of analysis, the column of the estimate type, frequency, detector temperature, sample size, etc., in the report. The data will be returned to the investigator, who will have the submitted value.

To assure that these samples do not change during the interim of transport from one lab to another, each lab will receive its own set of samples. Participating laboratories will be asked to return the samples within 30 days after receipt, for reanalysis in our laboratory. Results will be compared with data obtained before the samples were distributed. When they are returned, all samples should be identical. If any problems occur, the canisters can be refilled and reshipped, if necessary, because we now have ballast tanks — primary large quantity, high pressure standard of these materials in reservoirs.

So this is an area of activity. With all the different opinions represented here, however, reconciling the question you raise is very difficult. I feel quite confident that we can measure MCF and that we can do a pretty good job of it.

Dr. Schiff: On your N/S ratio, will you comment on the difference between your numbers and the NCAR values, and on that increase-with-time difference between you and Dr. Rowland?

Dr. Rasmussen: First, a background summary of our global trace halocarbon measurements might be useful. Measurement was begun in 1974. These GAMETAG profiles are from May and June 1978 in the Yukon; essentially the same flight profile was carried out in 1977. For GAMETAG we piggybacked on the NCAR study with several flights across the Atlantic to fill in some information gaps. We have a sample exchange program in Tasmania, New Zealand, and Samoa; in Barbados we are exchanging sample flasks to obtain further monthly values. At the same time, at Oregon Graduate Center we are directly responsible for day-to-day operation of the lifetime experiment sponsored by the Manufacturing Chemists

Association (MCA) at the Samoan and Tasmanian stations, where measurements are made 24 hours/day, 7 days/week; calibration of ambient samples is all electronically processed, and the data are shipped to us by the agent at the station. So it is a fairly integrated program.

Now, I will not give you numbers obtained from the real-time measurements at Tasmania, or Samoa, or Barbados; to focus on that program would be somewhat premature. However, it should be emphasized that the data we are obtaining in Samoa and Tasmania and those Peter Simmons and Jim Lovelock are obtaining in Barbados are entirely consistent with our sampling profile. The data are taken from low pressure samples obtained by directly flushing and pumping up a very well passivated and cleaned stainless steel bottle or from cryogenically collected samples accomplished by liquifying large parts of air into a small vessel, resulting in a very high pressure, large volume sample.

You asked about global concentrations and assessed numbers. Ratios between the NH and Southern Hemisphere (SH) can be confusing, because most values have been just arithmetic averages of what the investigator considered to be the concentration that best fits or represents the NH or SH. These products are prepared from a data bank of >100 data points. Time-weighting, when data were obtained within a given year, obviously caused some skewing, but these calculations provide an approximation of the main concentrations, as integrated for the volume of air in the NH and SH for these different years. The data, we believe, are real. We do have a good handle on the calibration, yet the small difference in MCF concentrations between 1976 and 1977 remains inexplicable at this time.

Dr. Schiff: Do you find altitude effects?

Dr. Rasmussen: In the original May 1975 flights from Alaska reported at a meeting in Greenbelt, Maryland, I did not doubt that — on individual flights, with carefully collected paired samples, between altitudes from 10000 to ~40000 ft (at the tropopause proper) — a ~3 percent falloff is observed in the level of MCF or these other four carbons, especially FC-11 and FC-12, because that was the entire focus of the experiment. I cannot attest to this on subsequent flights, because I was not present at all of them to oversee each of the measurements.

Dr. Schiff: Can you respond to this point? I was told you said that ground measurements and aircraft measurements differ by 30 percent.

Dr. Rasmussen: That is an error. I do not know where that statement arose.

Dr. Singh: The 1976 data I have seen for MCF show a ratio of not 1.23, but 2.2. What happened?

Dr. Rasmussen: This was arithmetic type. David Pierotti can speak to that.

Mr. Pierotti: We used data from 410 samples, not including the Helex data from continuous measurements on board ship. I am not sure of the reason for the difference, but one explanation may be the number of measurements. Our graph of 410 numbers is similar to graphs other people showed; however, they derived different NH and SH distributions. Other investigators used 13 or 17 numbers. I can use 13 or 17 numbers to pattern any distribution desired — from no change to a gigantic change. When 400 numbers are available, a better idea of the actual distribution can be patterned.

Dr. Singh: You haven't answered my question. Why was it wrong? In precisions like we are talking about, why was 1976 —

Dr. Rasmussen: Well, you are pushing on a sensitive point. You asked for it and I will give it to you. David Pierotti made the nitrous oxide (N_2O) measurements on the cruise. Joe Krasnec made the MCF measurements on the cruise. The experimental setup was operated on the same estimate with dissimilar columns and dissimilar values, so each investigator had control over his own system. Why the MCF data from the 1976 Helex cruise yield an average for other values I cannot testify, any more than I can explain why on the same flight Joe Krasnec and I obtained dissimilar values in our graph samples and cryogenic samples versus his real-time measurements.

Voice from Audience: I have all the original data, the original chromatographs, and I will review them. We do see longitudinal differences in MCF concentration, particularly in the NH, and certainly it could be that in a particular track of this cruise we were getting higher values in the NH.

Dr. Singh: This is very similar to what we have. I was curious and concerned: Jim Lovelock reported 2.2.

Dr. Rasmussen: I think it largely has to do with some ways in which the instrument was operated. Also, the value for the NH was skewed by the values taken shortly after leaving port in Los Angeles on the Helex en route to Peru. This was not a truly representative value for MCF in the NH. This has been one of our difficulties, and it is because of the large variability in MCF measurements between the latitudes of ~20° to ~60° N. I say these truly represent the mixing ratio in the NH. This may also relate to part of Dr. Schiff's misunderstanding concerning my rumored quote of a 30 percent difference between land-based samples and aircraft samples. Obviously, the land-based samples are collected at a latitude of ~45°.

Dr. Schiff: I was told that whenever you repeated measurements at the same place, by surface and by airplanes, you got different numbers. Is that true?

Dr. Rasmussen: No. We are currently testing this continental offshore effect again this week and for the next 2 weeks by piggybacking on the NCAR flight over the North Pacific, relating our findings to Hobb's cycle study, and by flying into and out of storm centers in the Gulf of Alaska. MCF values obtained on the Oregon coast will be compared with those obtained several hundred or a thousand miles offshore of the Pacific Northwest. At the same time, we will be intercalibrating and exchanging values with our colleagues at Washington State University (WSU). I don't think any difference exists in our MCF measurements on the coast of Oregon and their countryside measurements in eastern Washington. As of January 1979, the typical value for the station was ~135 ppt. I think Dr. Cronn said 123 yesterday, so I don't really see any great discrepancies.

Voice from Audience: Does the big difference result because our higher values were obtained over the North American continent and yours were obtained at the same latitude, at the same time, but over the Mid Pacific?

Voice from Audience: It looks like a latitude effect, but it really was a continent versus an ocean effect, because at 30° N they were over North America. South of that, they were over the Pacific. So it looked like a sudden jump at 30° latitude, but it was actually the effect of suddenly coming over the land, where all the MCF is emitted. The highest numbers, there, are all from North America.

Dr. Schiff: That kind of variation suggests a short lifetime, and that worries me. If you get those kinds of gradients over land masses, that indicates a very short lifetime.

Voice from Audience: There wouldn't be anything in the SH if that were true.

Dr. Schiff: Take a look at Joe Krasnec's curve, and take a look at the Rasmussen curve of the same flight. You see a very small gradient across the equator and a huge gradient peaking at ~50° N. A gradient like that certainly indicates a short lifetime.

Voice from Audience: I am sure that is a continental effect.

Dr. Schiff: Why the gradient over the continent, unless our Eskimos are using a hell of a lot of MCF?

Voice from Audience: This is on the same flight.

Dr. Crutzen: I would like to comment on the latitudinal cross section displayed yesterday. In the two-dimensional modeling effort, I also found that ground-level MCF mixing ratios reach a maximum around 50 to 60° latitude, and this may relate to a first issue to be considered in resolving discrepancies. The emission per unit area, I think, is one factor which we may easily forget.

After all, the surface area at 60° is smaller than at 40°. Also, the destruction rates of MCF are much smaller at those latitudes. This raises the possibility that photochemical effects play an important role.

Dr. Schiff: Perhaps the differences can be explained, but I am trying to play the devil's advocate to discover if real discrepancies in the measurements do exist.

Dr. Crutzen: May I read a few lines from this handout on Leroy Heidt's and Joe Krasnec's experimentation:

> The graph sample analysis in the past 2 years confirms the problem involved with the integrity of grab air samples. Methyl chloroform and carbon tetrachloride could not be measured accurately in the past due to the absorption problems on the inner surfaces of the sampling vessels. Difficulties in making reliable methyl chloroform measurements also involve choice of materials for sampling containers — stainless steel, aluminum, or glass, etc. — and sampling system contamination by pumps, inlet systems, etc. For these reasons the group is making measurements on the ground and in the air. No pumps are used in the all-stainless-steel GC sampling system. Finally, another difficulty encountered in the course of making long term methyl chloroform measurements is the stablity of calibration standards.

Now, this comes back to what you just said. Significant changes (in this case, decreases) were observed in the concentration of different calibration mixtures over a period of several months. One solution appears to be the storage of secondary calibration mixtures in larger vessels and under high pressure — several hundred psi. Also, preparation of primary standards using dynamic dilution techniques appears to be the preferred method.

Dr. Rasmussen: I would like to comment on the stability of these vessels. The vessel in which Heidt and Krasnec are observing absorption on the wall is typically the NCAR high vacuum, ultra clean canister, which draws in an ambient sample through the probe system on the aircraft. At our March 1976 halocarbon workshop we discussed ad infinitum the difficulties of obtaining reliable stability in evacuated canister samples. There is a host of examples in which everything disappeared, even FC-11 and FC-12, in some of these evacuated canister samples. The samples we use are pressurized typically to ~30 psi in the grab sample phase, and we have never had any problems with stability in the electro-polished, passivated, stainless steel vessels. These vessels, which I prepared and developed at WSU, are used extensively by people at WSU; at SRI they are purchased from a small machine company in Pullman that was our manufacturing outlet. Have you had any problems with MCF and these stainless steel vessels?

Dr. Singh: We have not seen any deterioration, but we have had some unexplained problems, so the integrity, I suppose, could go either way.

Dr. Schiff: I don't think it is a matter of pressurizing or not, because I think Dr. Rowland will say that he can get integrity with samples that are evacuated.

Dr. Rowland: Pressurizing involves the possibility of contamination.

Dr. Schiff: I don't think any problem can be traced to pressurizing or not pressurizing. In reference to the comment that you are getting good agreement with Jim Lovelock, I would like to mention a letter from Jim Lovelock, dated 9 January 1979, in which he states, "I am not surprised that there are uncertainties about atmospheric abundance of the MCF. It is very difficult to prepare standards of it because of the reactivity."

Dr. Rasmussen: Well, Jim Lovelock is telling you things he is not telling me.

Dr. Schiff: Now, can we hit a couple of these other points? Dr. Rowland, maybe you would like to comment on the increase of MCF with time, and, Dr. Rasmussen, on your trend of the NH/SH ratio. As I remember, you found the interhemispheric ratios were rapidly approaching one another. Is that still the case?

Voice from Audience: That was, I think, at 45° N versus Antarctic ratio.

Dr. Schiff: NH/SH ratios are coming closer to unity with time.

Dr. Rasmussen: These data from the World Meteorological Organization meeting have been updated to January 1979. As David Pierotti said, these were comparisons between the average representative concentration of those species for the month of January each year, characterizing the specific Northwest, typically 45° N, and the values that we were obtaining at the South Pole, typically 90° S. It is a very simplistic comparison of the arithmetic mean measurements, typical of January of the appropriate year. In the MCF measurements from 1976 to 1979, it can be seen we have maintained continuity and consistency in the calibration comparable to the consistency we maintained at WSU, where the standards were originally prepared. As far as I know, no drift at either laboratory can be seen in the ratio of 1.72, 1.53, 1.38, and 1.42 of the NH/SH maximum difference, as contrasted in these two sites where the analyses were made. These are not hemispheric averages. They are not integrated for the hemispheric burden.

Dr. Schiff: The point is they are coming closer.

Voice from Audience: Between 1976 and 1977 the ratio appeared to drop, and I am not sure why.

Dr. Schiff: Would you like to comment on that difference in time, Dr. Rowland?

Dr. Rowland: We don't have a long series of data. All we have are South America data from a period 8 or 9 months apart. There is a difference, of course, to a value of 9 percent. That is not a rigorously accurate figure.

Dr. Schiff: You are saying there is no significant difference between your numbers and theirs?

Dr. Rowland: Since their numbers fluctuate sufficiently from one year to the next, I doubt that a significant difference exists.

Dr. Rasmussen: I think the data we heard this morning from the manufacturers, describing a relatively small increase in total production of MCF during the last few years, are fairly consistent with our observations. However it is a very limited data base.

Dr. Singh: It is not consistent with the emission data you have available.

Dr. Rowland: Using the Dow Chemical emission data, going N to S, in conjunction with any of these removal rates in the NH and SH and the day rate of mixing between the hemispheres, yields a ~1 percent/yr increase over the last 3 yr. Values for a lifetime of 8 to 12 yr are not important here; the Dow emission data feed into a number on the order of 12 or 13.

Voice from Audience: I heard two people this morning say that the MCF production levels scarcely changed during the years 1976 to 1978. I heard two different people mention a figure like 630 million.

Dr. Rowland: That is U.S. production, rather than emission.

Dr. Schiff: Is there a big difference?

Dr. Singh: The U.S. has a global difference and it does not amount to a ratio.

Dr. Rowland: None of us has any emission data.

Voice from Audience: It hasn't increased in the U.S. Has it increased that rapidly in the rest of the world in the last 2 yr?

Dr. Rowland: You will have to get the answer from Dow Chemical.

Voice from Audience [*Dr. Farber?*]: Does somebody want me to comment on the Dow data? In the little paper that I sent to all the attendees I knew were coming, Figure 3 shows our best estimate of emission. In some cases, we subtracted inventory we knew to be building up, and we subtracted what we thought would go to chemical use or be not emitted. This estimate is probably accurate to within 5 to 10 percent, based on the fact that we think we know more about the use and production of the product than anybody else. I don't know anything about Russian production.

Voice from Audience: What are the figures for 1976, 1977, and 1978?

[*Dr. Farber?*]: In 1976 the world emission of FC-111 was estimated at 894 million lb; in 1977 it was ~981 — a ~10 percent increase. In 1975 it was 764; in 1974 it was 871, reflecting a decrease in 1975.

Voice from Audience: As with most other chemicals, this was caused by economic conditions.

Voice from Audience: What was 1978?

[*Dr. Farber?*]: It was close to 1 billion lb in 1978. Dr. Neely, do you know what the number was?

[*Dr. Neely?*]: A little over 1 billion.

[*Dr. Farber?*]: Less than 1.1, anyway.

[*Dr. Neely?*]: 3 or 4 percent, maybe.

[*Dr. Farber?*]: Yes, that is our estimate. The U.S. numbers are: 1974, 495; 1975, 443 (again, that reversal due to economics); 1976, 487; 1977, 521; and I don't have the 1978 number.

Dr. Singh: I would like to make a comment on Eastern Europe and the Soviet Union. I have nothing to report other than a very qualitative statement that MCF emissions are extremely low. The estimate is something like 2 percent.

Voice from Audience: Are any SH data available?

Voice from Audience: I don't have the figures for MCF, but I looked at a document on FC-11 and FC-12 which showed where they were sold and assigned by latitude, and so on. About 10 yr ago, the amount sold in the SH was ~3 percent. By 1973 to 1974, it had increased to maybe 4 percent: manufacturing of FC-11 and FC-12 in the SH had started. So FC-11 and FC-12 have been increasing to as much as 8 percent in the SH now, but I have no corresponding figures for MCF.

Dr. Singh: Our model calculations may be 4 percent.

Voice from Audience: Four percent — that is probably good enough.

Voice from Audience: My estimate for fluorocarbons is 90 percent between 30 to 50° N, 5 percent N of that, 2 percent between 30° N and 30° S, and 3 percent from 30 to 40° S.

Dr. Singh: Four percent?

Voice from Audience: Yes, 4 percent would be right.

Dr. Schiff: Are there any other comments about the measurement aspect of the problem?

Voice from Audience: It seems that several representative measurements have been discussed under this general question. Do the investigators feel there is enough quality assurance in calibration for this sort of thing?

Dr. Schiff: I think the consensus is that there is not. I think what you are saying is that everyone feels his own accuracy is quite high; however, the figures given here reflect a bigger spread than the sum of the accuracies cited. For instance, the NH value numbers we have heard have ranged from 94 to 145, although accuracies within ±10 are claimed.

Dr. Rasmussen: We are "mixing apples with oranges." The interlaboratory calibration published on MCF this past year said that, among the laboratories measuring these standards, the spread was pushed from -39 percent around the submitted value of 100 ppt. Enough samples came back with something left in those canisters to verify that we were at the 100 ppt level on the return sample. I have described our estimated absolute accuracy according to Peter Simmons, Jim Lovelock, Paul Fraser, and myself. The only other laboratory that I would include in that is the WSU laboratory, because I feel fairly confident in their capability to make these measurements.

Now, I preface this by stating our general good agreement on halocarbons with NOAA, the Paul Golden laboratory, and the one previously operated by Thompson. On the other hand, on three different occasions, irreconcilable calibration problems arose between my laboratory and NCAR's laboratory, and at the halocarbon workshop, where we made these onsite sample analyses in Paul Golden's laboratory. Again, we have problems reconciling the values that Leroy Heidt presented; you were at the meeting, Dr. Schiff, and can testify whether that is an overstatement or understatement of fact. This was the second or third week of March 1976; David Pierotti and Joe Krasnec had just come back from the Helex cruise. The 10 percent described does not reflect what the field analysts, in general, can achieve, and it does not describe overall results among laboratories. The presentations reflected many differences to be reconciled.

Dr. Schiff: The "apples" that I am comparing are the "apples" of this group, who are measuring in the clean atmospheric air. I am saying that the spread between the numbers we have seen is greater than the sum of the accuracies claimed by the individual group. That, I think, is a real problem. I think we have to somehow resolve it. I also am rather disappointed that we do not have represented here (other than what Dr. Crutzen read) the groups who are having real difficulty and who are claiming that they cannot calibrate with an accuracy of 50 percent and cannot get standards with 50 percent reproducibility. So I am sorry that Leroy Heidt and Joe Krasnec and Art Schmeltekopf are not here. I am also rather sorry that Doug Davis isn't here, since he was responsible for the GAMETAG flight structured with two groups measuring the same latitudinal region. My summary of the situation is that we have groups here who claim they can measure MCF, and there are differences among them — I mean real differences. I think there are also groups that aren't represented here who have found even greater differences.

Dr. Singh: The subtle differences that we are talking about ought to be put into some perspective. We have 100 ppt in the temperate latitudes and a lifetime calculation of 6 to 12 yr. As long as we understand that, the decisions ought to be made on that. So from a scientific point of view, sure, we have all these problems, but they all point to this narrow range.

Dr. Schiff: I think you are quite right. In the regulatory community, decisions can be based on present atmospheric concentrations of MCF, and, of course, I am not suggesting any critical difference between 94 and 135 ppt. But to go beyond that, it is important that we at least know where we stand in the scientific community with respect to our ability to measure MCF and with what kind of accuracy. At the moment, I do not feel I have a solid and reliable answer to this question.

Voice from Audience [*Mr. Pierotti?*]: I would like to comment on the differences in standard deviations in the measurements. Our 1976 measurements in the NH range from 160 to ~80. That is a factor of 2, a significant difference, and that is with all the same sampling methods and the same standards.

Dr. Schiff: In clean air?

[*Mr. Pierotti?*]: It is difficult to know what you mean by "clean air." Is there any "clean air" over North America or over the Atlantic Ocean? We measured a lot of other compounds, too. In cases where everything is elevated (the fluorocarbons, for example), analysis is possible. But I think the differences occur because some people have a very small data base that will fit an unlimited variety of distributions.

Dr. Schiff: If, indeed, there is a big variation of a factor of 2, then it is saying something very real about the lifetime of that compound.

Dr. Rowland: If there is a difference between taking 13 points out of 400 and 13 out of 13. We collected 7 samples in South America and analyzed them in the laboratory. The spread of deviation for MCF in those was 65 ±2 for the same sample in 7 different locations taken over a period of ~1 week. The measurements repeated for a several-month period showed no appreciable deviation, and it looks as though we took 7 samples out of the same year. Now, that is not very many data points, but there is no spread at all. I suspect that is what you can get, if you pick up oceanic samples that have no contamination.

Dr. Schiff: And I worry about that factor of 2 spread in the so-called "clean air." If it is true, then that compound must have a very short lifetime.

Dr. Singh: When you talk about spread related to lifetime — in this case, where the emission sources are very narrow — I would not necessarily jump to that conclusion too quickly.

Dr. Schiff: I would argue that with you. Consider, for instance, that the air mass you measure today at a given location may have come from a different place — and yet you are still saying it is "clean air," not contaminated air, and that the measured values can only reflect a latitudinal dependency.

Dr. Singh: I see a number of data points, and the distributions are very similar.

Voice from Audience: Well, our numbers and yours are very close.

Dr. Singh: We have measured in two different longitudes, and — perhaps because of the mixing differences in the two hemispheres and perhaps because of the seasonal differences — there are some real changes in these distributions. None of us is really sure of the sections of the two hemispheres that have been done at one point in time. I think that should be stressed, and some of these differences, perhaps, are real.

Voice from Audience: I agree. The distribution seems too complex, and in particular does not seem to square with the idea of a long lifetime. It is surprising and it does seem to point to something we don't understand about the behavior of MCF in the atmosphere. It tells us we don't know as much as we think, perhaps.

Dr. Schiff: That may be a good note to end on.

Dr. Rasmussen: I would like to make sure that no one copies this figure of 137 ±55 for November. That is a typo; it is ±15. The ±1 σ for 45° N is real, and it is always ±10 to 15 ppt for MCF at that site. We made a few fluorocarbon measurements at this site, and they are exceedingly constant. Much more variability in MCF is seen than in the fluorocarbon measurements or in the SH. Those data are ±5 to 7 at Samoa and ±4 to 6 at Tasmania. I agree with you, Dr. Rowland, that when you get into the SH and Antarctica, you could get this very tight tolerance; in the NH, however, we don't get a tight tolerance on MCF measurement.

Dr. Rowland: Let me say one other thing. We spent about as many manhours, I suspect (or close to it), and we have very few points. They are looking at a different kind of measurement, and they are collecting many measurements over a wide area. We are focusing on one particular thing and spending time striving for better accuracy. We have different aims. I don't think, from the point of view of a regulatory agency, that it makes any real difference whether it is 100 or 135.

Dr. Schiff: No, I don't think so either, although I want to stress that measurements are important and measurements are not getting enough exposure at this meeting. I wouldn't like to see EPA walk away thinking that we have got the measurement game well in hand. I think there are still some unanswered questions, and that is the only message I wanted to get across.

Voice from Audience: I agree that perhaps we can explain the variability in some of these data by the possibility that the residence time is much shorter than earlier estimated. I think that needs to be investigated.

Dr. Rowland: A variability should, therefore, exist in every place. If you measure the variability of the SH and it is not the same as in the NH, then you cannot suggest a short residence time. To state a real variation in the model, you must see it every place.

Voice from Audience: May I make one other comment to which Dr. Singh may want to respond, because it concerns his data? I think that something can be neglected here, which not only has to do with these measurements, but with all measurements of trace contaminants. When something is 3 or 4 days away, that is damn hard to prove. Talk to other experts. Talk to the meteorologist in this field. In any bit of data I study, I don't see (with some exceptions) this projectory analysis. Trifluoroethylene shows up in remote sites. Even in the OH-trichloroethylene kinetics, the O_3 type, or the smog change, it shouldn't be there, as far as I can see. Why is it there, if it isn't a contaminated air mass to some extent? Would you want to comment on that?

Dr. Singh: I agree with you.

Dr. Schiff: Well, thank you. Thank you all for coming.

Dr. Hanst: Well, we devoted the Panel Discussion to one topic. Mrs. Bishop has asked if it wouldn't be possible for a summation. I was thinking of something Dr. Molina told me, and this might close it out. When we look at the different molecules and count the Cl, that is one indication of the degree of danger to the stratosphere: the combination of Cl and lifetime. FC-11 holds the greatest danger (FC-11 has three Cl, FC-12 has two, and fluorocarbon-22 (chlorodifluoromethane, $CHClF_2$) has only one), and they all have the same lifetime in the air. Then that is the direction we should go in; that is the summation.

APPENDIX A

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